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2014

JIRA KONGPRAN

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and Japan, and their Distribution to Water Environment**

JIRA KONGPRAN

Doctoral Dissertation

Course in Environmental Management
Graduate School of Global Environmental Studies
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Abstract

Perfluoroalkyl caboxylates (PFCAs) is one of the most concerned groups of PFCs due to their persistent, bio-accumulative and toxic properties, and they were widely detected in environment, wildlife and human (Fujii *et al.*, 2007; Lau *et al.*, 2007). Aquatic environment is believed to be main transport pathways and ultimate sinks of PFCAs (Ahrens, 2011); however, their detection in remote areas raised concerns of atmospheric contamination. Fluorotelomer alcohols (FTOHs) are recognized as volatile precursor compounds of PFCAs in environment. FTOHs were detected in air of several developed countries and along the Arctic, Atlantic and Southern Oceans. However, sources and transport pathways of PFCAs and FTOHs in air environment have not been well understood and very few studies have been conducted in developing countries.

This study conducted air sampling at fourteen outdoor and indoor sites in Thailand using the high volume air sampler. Three FTOHs (*i.e.* 6:2 FTOH, 8:2 FTOH and 10:2 FTOH) and eight PFCAs (*i.e.* PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA and PFDODA) in air samples were analyzed using GC-MS and HPLC-MS/MS, respectively. FTOHs (1,690-13,030 pg/m³) and PFCAs (4-110 pg/m³) were detected at every sampling site in Thailand, which illustrated their contamination in the study areas. 10:2 FTOH (26-76%) and 8:2 FTOH (14-55%) were dominant compounds among FTOHs, whereas PFOA (9-72%) and PFHxA (3-50%) were the dominance among PFCAs. FTOHs were mainly distributed in gas-phase fractions (89-100%). However, the particle-phase of FTOHs was increased with the increase of fluorocarbon chain length. From the study, particle-phase of 6:2 FTOH, 8:2 FTOH and 10:2 FTOH was partially detected in 14%, 43% and 46% of the samples, respectively. Inhalation intakes of airborne FTOHs and PFCAs were calculated to assess human exposure. In mean scenario, the intake of FTOHs and PFCAs in adults was 0.636 ng/kg-day and 0.004 ng/kg-day, respectively. Additionally, it was found that inhalation intake of PFOA (0.002 ng/kg-day) was a minor exposure, compared to the intakes by water drinking (0.190 ng/kg-day) and food consumption (0.175 ng/kg-day). However, airborne FTOHs were detected about two orders of magnitude higher than PFCAs. Therefore, FTOHs

have high possibility of contribution to PFCAs contamination in environment and contribution to PFCAs exposure by their precursor compounds. This result showed the first investigation of FTOHs and PFCAs in air of Asian developing countries. Compared to the results in developed countries, outdoor FTOHs concentrations in Thailand were found in higher level in most of sampling sites. In Thailand, the highest outdoor concentration of FTOHs ($11,850 \text{ pg/m}^3$) and PFCAs (110 pg/m^3) were found at an industrial wastewater treatment plant, which indicated their sources from industrial sectors.

Focusing on industrial sources of airborne FTOHs and PFCAs, air sampling was also conducted In Japan. Significant high concentrations of FTOHs and PFCAs in air were detected at a fluorotelomer compounds production industry ($588,000 \text{ pg/m}^3$ and $604,000 \text{ pg/m}^3$, respectively) which were four to five orders of magnitude higher than those in a remote site (130 pg/m^3 and 25 pg/m^3 , respectively). High concentration of FTOHs ($219,000 \text{ pg/m}^3$) was also detected in an industry which using fluorotelomer compounds in their production process. These results indicated importance of industrial sources of FTOHs and PFCAs emission to atmosphere. Compared to previous studies in Japan and other countries, the results in this study showed the highest concentration of FTOHs and PFCAs which have been reported in air environment. Not only in particle-phase but PFCAs were also detected in gas-phase in the industrial sources. FTOHs were dominant in gas-phase fractions (77.9-100%) whereas PFCAs were mainly detected in particle-phase (73.4-99.8%). Most of correlations between particulate FTOHs/ PFCAs and total particulate matter were strong ($R>0.7$). These results indicated that FTOHs/ PFCAs enriched particles emission from industrial sources. Total inhalation intake of FTOHs and PFCAs found from the fluorotelomer compounds production industry was 206 ng/kg-day for mean scenario and 876 ng/kg-day for worst scenario, which were remarkably high and exceeded recommended guideline by Japanese government (300 ng/kg-day for PFOA). Activated carbon air cleaner has been applied to remove airborne FTOHs and PFCAs in this industry. Higher reduction rates were observed for FTOHs (48-88%), compared to PFCAs (3-53%).

To illustrate distribution pathways of FTOHs and PFCAs from air to water environment, air and rainwater samples were collected at Kyoto University, Japan. All PFCAs were

detected in every air (90-190 pg/m³) and rainwater (7.3-28.7 ng/L) sample, indicating their distribution from air to water *via* wet deposition. Total flux of PFCAs ranged between 120-1,830 ng/m². PFCAs in rainwater were dominant in liquid-phase (71-92%), while solid-phase partitioning increased with increasing of fluorocarbon chain length. PFCAs concentration in rainwater in Kyoto, Japan was higher than those in most of the previous studies. All FTOHs were detected in the air (770-2,820 pg/m³) but they were below the detection limits in rainwater (<6.9-8.7 ng/L). This result indicated that FTOHs were difficult to be wet deposited from the air. Most of PFCAs in rainwater samples increased after a few weeks of sunlight exposure (18-186%). Similar to the results in Japan, increases of PFCAs (9-373%) were obtained by river water samples which exposed to sunlight in Thailand. These results indicated the photodegradation of their precursor compounds in water environment by natural sunlight.

Photodegradation of 8:2 FTOH was confirmed by a UV (254 nm) irradiation experiment. 8:2 FTOH was fast degraded under UV light without any photo-catalysts. After 24 hours of irradiation, 8:2 FTOH was not detected at the initial concentrations of 2.16 nmol/L and 21.6 nmol/L, but remained 1.63% of the highest initial concentration (216 nmol/L). First-order kinetic was used to simulate photodegradation of 8:2 FTOH and the rate constants were 0.228, 0.298 and 0.188 hour⁻¹ for the initial concentration of 2.16 nmol/L, 21.6 nmol/L and 216 nmol/L, respectively. Five PFCAs with the length of 5 to 9 carbon chain were formed as degradation products of 8:2 FTOH for all three initial concentrations. Within 24 hours of UV irradiation, the highest production rate of PFCAs was 1.76%, 1.79% and 1.02% for above-mentioned initial concentrations respectively. Additionally, it was found that under the SCAN mode of HPLC-MS/MS, not only PFCAs but also several compounds *i.e.* fluorotelomer acids, fluorotelomer unsaturated acids and fluorotelomer olefins were identified as degradation products of 8:2 FTOH.

Keywords

Air environment, Fluorotelomer alcohols, Japan, Perfluoroalkyl carboxylate, photodegradation, Thailand, Wet deposition

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Abbreviations

AC	air cleaner
ACF	activated carbon fiber
ACN	acetonitrile
Ave	Average
BW	body weight
CECs	contaminants of emerging concerns
EIC	extracted ion chromatogram
FTCAs	fluorotelomer acid
FTOHs	fluorotelomer alcohols
FTUCAs	fluorotelomer unsaturated acids
GC	gas chromatography
GFF	glass fiber filter
HPLC	high performance liquid chromatography
IDL	instrument detection limit
IQL	instrument quantification limit
MDL	method detection limit
MQL	method quantification limit
MRM	multiple reactions monitoring
MS	mass spectrometer
MS-MS	triple quadrupole mass spectrometer
MTBE	methyl tetra butyl ether
PCD	pollution control department
PE	polyethylene
PFASs	perfluoroalkyl sulfonates
PFCs	perfluorinated compounds
PFCAs	perfluoroalkyl carboxylates
PFDA	perfluorodecanoic acid
PFDODA	perfluorododecanoic acid
PFHpA	perfluoroheptanoic acid

PFHxA	perfluorohexanoic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorinated sulfonic acid
PFPeA	perfluoropentanoic acid
PFUnDA	perfluoroundecanoic acid
POPs	persistent organic pollutants
PP	polypropylene
PUF	polyurethane foam
RA	residential area
RT	retention time
SIM	selective ion monitoring
SIP	sorbent-impregnated polyurethane foam
TDI	tolerable daily intake
THC	total hydrocarbon
TIC	total ion chromatogram
TPM	total particulate matter
QFF	quartz fiber filter
UV	ultraviolet
VOCs	volatile organic compounds
WWTP	wastewater treatment plant

Chapter 1

Introduction

1.1 Research Background

Many substances are produced and used for industrial applications but later contaminated and caused risk to environment and human being. Perfluorinated compounds (PFCs) are known as persistent organic pollutants (POPs) and contaminants of emerging concern (CECs) due to their persistence, bioaccumulation and toxicity. Moreover, they were ubiquitous detected in environment. Large volume of PFCs have been produced since the 1950s and widely used as processing additive during fluoropolymer productions, and surfactants in consumer products but the environmental concerns have arisen since 2000 (UNEP, 2009; Ahrens, 2011; US.EPA, 2013).

Perfluoroalkyl carboxylates (PFCAs) is one of the most concerned groups of PFCs which were widely detected in water, sediments, soil, plants, wildlife and human (Fujii *et al.*, 2007; Lau *et al.*, 2007). However, their sources, fate and transportation in the environment have not been well understood yet. Aquatic environment is believed to be main transport pathways and ultimate sinks of PFCAs (Ahrens, 2011) but they were also detected in biological samples from remote locations (Houde *et al.*, 2005; Smitwick *et al.*, 2005; Schiavone *et al.*, 2009), as well as in snow samples of the Arctic which atmosphere is solely their contamination sources (Young *et al.*, 2007). Therefore, atmosphere is suggested as an important environmental compartment for global contamination of PFCAs. Fluorotelomer alcohols (FTOHs) are recognized as indirect sources of PFCAs in remote areas due to their volatility and degradability properties. Importantly, FTOHs are high volume production chemicals (Styler *et al.*, 2013) among other fluorotelomer compounds and recently, their detection were reported in air environment in several developed countries, including in the atmosphere above the Arctic, Atlantic and Southern Oceans. These raise more concerns on contamination and distribution of FTOHs and PFCAs in the atmosphere.

Information on contamination of FTOHs and PFCAs in air environment has been accumulated, but it is mainly in developed countries while very few studies have been conducted in Asian developing countries. In addition, their sources and behaviors in air, and distribution pathways to other environmental compartment are limited. Further research is needed to better understand their contamination in environment and potential risks to human.

1.2 Research Objectives

Main objective of this research is to study contamination of fluorotelomer alcohols (FTOHs) and perfluoroalkyl carboxylates (PFCAs) in air environment and their distribution to water environment. The specific objectives are as follows;

- (1) To develop analytical methods of FTOHs and PFCAs in air samples and investigate their contamination in outdoor and indoor air in Thailand
- (2) To investigate industrial sources of airborne FTOHs and PFCAs in Japan and their countermeasures using air cleaner
- (3) To examine distribution pathways of airborne FTOHs and PFCAs by wet deposition and photodegradation in water environment
- (4) To elucidate photodegradation rates and products of 8:2 FTOH by conducting a UV irradiation experiment

Framework of the study is shown in **Figure 1.1**. This dissertation consists of seven chapters including introduction (chapter 1), literature review (chapter 2), contamination of FTOHs and PFCAs in air environment in Thailand (chapter 3), industrial sources of airborne FTOHs and PFCAs in Japan (chapter 4), distribution pathways of airborne PFCAs and FTOHs to water environment by wet deposition and degradation (chapter 5), photodegradation rates and products of 8:2 FTOH (chapter 6), and conclusions and recommendation (chapter 7). Scope of the study related to each chapter is shown in **Fig. 1.2**.

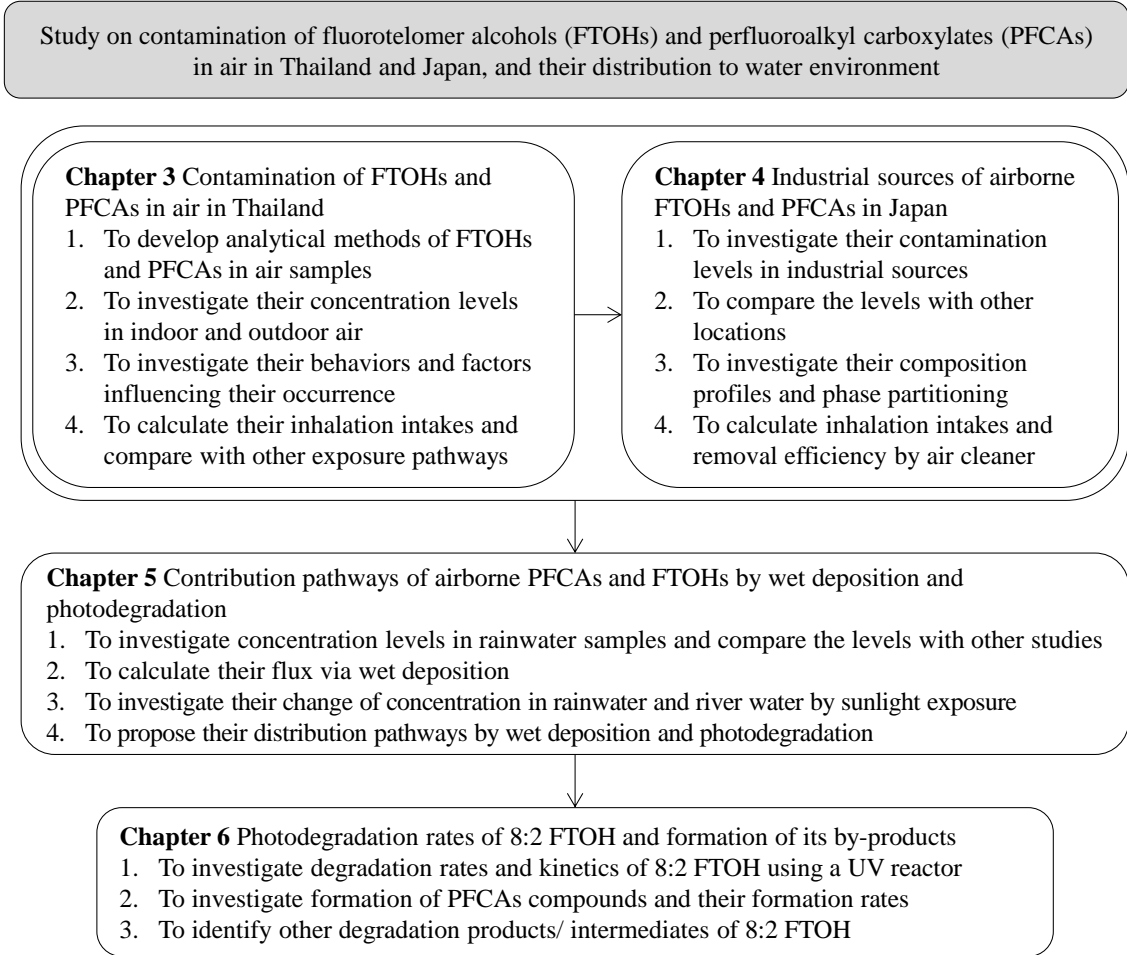


Figure 1.1 Framework of the study

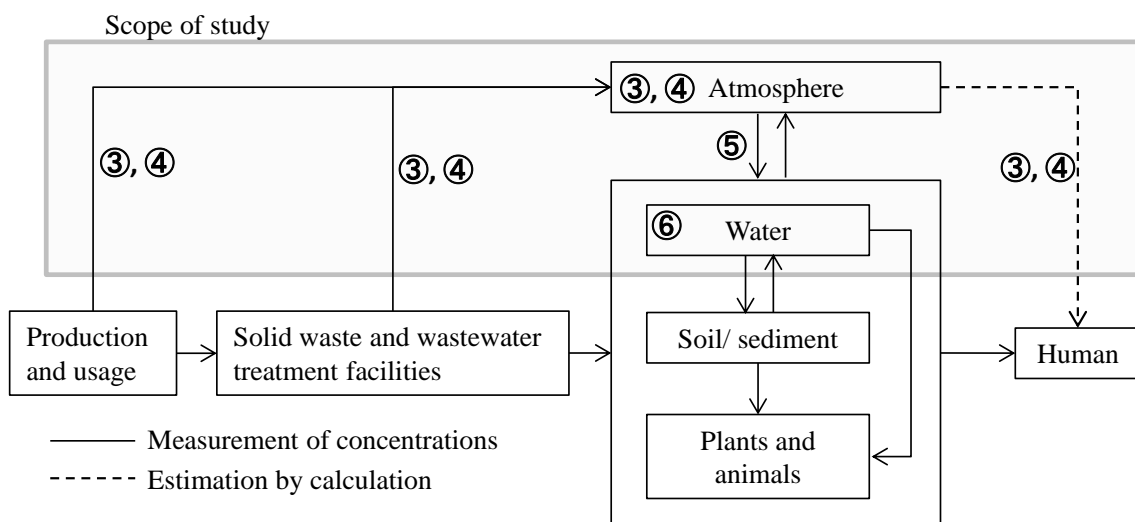


Figure 1.2 Scope of the study

Chapter 2

Literature Review

2.1 Introduction to PFCAs and FTOHs

Perfluorinated compounds (PFCs) are synthetic chemicals, consisting of a fluorocarbon chain and a functional group (*e.g.* a sulfonic acid, a carboxylic acid, an alcohol, a phosphoric acid, *etc.*). At present, several hundreds of these compounds are known (OECD, 2007). Since 2000, two classes of PFCs *i.e.* perfluoroalkyl sulfonates (PFASs) and perfluoroalkyl carboxylates (PFCAs) have been intensively concerned due to their persistent, bioaccumulative and toxic properties, and they were widely detected in environment. As a result, PFASs related compounds *i.e.* perfluorinated sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride (PFOSF) were added to Annex B in Stockholm Convention on Persistent Organic Pollutants (POPs) in May 2009 (UNEP, 2009), subjecting them to restrictions on production and use. However, other PFCs still being produced and used, which further investigation on their contamination levels and pathways in environment are needed. This study focus on PFCAs and their precursor compounds *i.e.* fluorotelomer alcohols (FTOHs). Chemical structures of these target compounds are shown in **Table 2.1**. PFCAs consist of a fluorocarbon chain and a carboxylic acid group, while FTOHs consist of a fluorocarbon chain and an ethanol moiety.

2.1.1 Production and Use

PFCs are surface active substances with an extreme low surface tension, and they repel water, grease and dirt. Large volume of these compounds have been produced since the 1950s and widely used as processing additive during fluoropolymer productions, and surfactants in several industrial and consumer products (Danish EPA, 2008; UNEP, 2009; Ahrens, 2011; US.EPA, 2013).

Table 2.1 Chemical structures of target compounds in this study

Perfluoroalkyl caboxylates (PFCAs)	Fluorotelomer alcohols (FTOHs)
$ \begin{array}{c} \text{F} \quad \left[\begin{array}{c} \text{F} \\ \\ \text{C} \\ \\ \text{F} \end{array} \right]_n \\ \quad \quad \\ \text{F} \quad \quad \text{F} \end{array} \text{---C---C---C} \begin{array}{c} \text{O} \\ // \\ \text{OH} \end{array} $ $\text{CF}_3(\text{CF}_2)_n\text{COOH}$	$ \begin{array}{c} \text{F} \quad \left[\begin{array}{c} \text{F} \\ \\ \text{C} \\ \\ \text{F} \end{array} \right]_n \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \quad \quad \\ \text{F} \quad \quad \text{F} \quad \quad \text{H} \quad \quad \text{H} \end{array} \text{---C---C---C---C---OH} $ $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$
$ \begin{array}{c} \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \\ \quad \quad \quad \quad \quad \quad \\ \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \end{array} \text{---C---C---C---C---C---C---C---C} \begin{array}{c} \text{O} \\ // \\ \text{OH} \end{array} $ <p><i>e.g.</i> Perfluorooctanoate (PFOA)</p>	$ \begin{array}{c} \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \\ \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{F} \quad \text{H} \quad \text{H} \end{array} \text{---C---C---C---C---C---C---C---C---C---C---OH} $ <p><i>e.g.</i> 8:2 fluorotelomer alcohol (8:2 FTOH)</p>

PFCAs are usually manufactured by electrochemical fluorination process (ECF) (Fiedler, 2010). During the manufacturing process, an electric current is passed through hydrogen fluoride and therein dissolved or dispersed organic compounds. All hydrogen atoms of those organic compounds are replaced by fluorine. PFCAs are used for manufacturing fluoropolymer (such as Teflon®) (Danish EPA, 2008). The global historical production of PFCAs during 1951-2004 were estimated to be 4,400-8,000 tonnes (Prevedouros *et al.*, 2006).

FTOHs are produced by telomerization process, which perfluoroalkyl-ethyl iodides are synthesized and after that iodide is replaced by a hydroxyl group (Fiedler, 2010). Production of FTOHs has increased world-widely, particularly for fluoropolymers and surfactants used in carpet, textile and paper treatment, as well as for paints, coatings and adhesives. During 2000-2002, they were produced 5,000-6,500 tons per year and increased to 11,000-14,000 tons in 2005 (DuPont, 2002; Dinglasan and Mabury, 2006), which are considered as a class of high volume production chemicals of PFCs (Styler *et al.*, 2013).

2.1.2 Physico-chemical Properties

PFCAs are persistent compounds due to a very strong of carbon fluorine bond (≥ 450 kJ/mol) (Fiedler, 2010). They have high water solubility, moderate sorption onto particles and very low volatility (Conder *et al.*, 2008; Kwok *et al.*, 2010). In contrast to PFCAs, FTOHs are degradable and volatile. FTOHs have high vapor pressure and low water solubility, compared to PFCAs. These properties indicate that FTOHs will be found mostly in gas-phase (Gauthier and Mabury, 2005). Physico-chemical properties of PFCAs and FTOHs are shown in **Table 2.2**.

2.1.3 Overview for Sources and Contamination Pathways in Environment

PFCAs can be released to the environment from fluoropolymer manufacturing industries. They can also occur as impurities in products of fluoropolymer and as degradation products of fluorotelomer compounds. The majority emission sources of PFCAs (80%) are from fluoropolymer manufacturing and use (Prevedouros *et al.*, 2006). Wastewater treatment plants are known as point sources for PFCAs in the rivers (Vierke *et al.*, 2011). A small contribution to PFCAs in the environment is from abiotic (*e.g.* atmospheric) and biological degradation of precursor compounds (Wang *et al.*, 2009).

PFCAs were widely detected in a variety of environmental media; including surface water (rivers, lakes, and oceans), groundwater, tap water, rainwater, snows, sediments and soil, and were also detected in animal, plant and human tissues (Fujii *et al.*, 2007; Lau *et al.*, 2007; Fiedler, 2010; Fromme *et al.*, 2009). Aquatic environment is believed to be main transport pathways and ultimate sinks of PFCAs in environment (Ahrens, 2011) as shown in **Fig. 2.1**. However, their sources, fate and transportation in the environment have not been well understood. PFCAs, especially perfluorooctanoate (PFOA), were detected in biological samples from remote locations (Houde *et al.*, 2005; Smitwick *et al.*, 2005; Schiavone *et al.*, 2009), as well as in snow samples of the Arctic which atmosphere is solely their contamination sources (Young *et al.*, 2007). Therefore, atmospheric transportation and degradation of their precursor compounds is suggested as an important pathway for global contamination of PFCAs.

Table 2.2 Physico-chemical properties of target compounds in this study

Compounds	MW	Chemical formula	CAS No.	Solubility (g/L)	pK _a	pH	Melting point (°C)	Boiling point (°C)	Vapor pressure (Pa)	Octanol-air partitioning (Log K _{oa})	Octanol-air partitioning (Log K _{ow})
Perfluoropentanoic acid (PFPeA)	264	CF ₃ (CF ₂) ₃ COO ⁻	2706-90-3	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	82 (85 mm Hg)	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>
Perfluorohexanoic acid (PFHxA)	314	CF ₃ (CF ₂) ₄ COO ⁻	307-24-4	15.7	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	157	<i>n.a.</i>	<i>n.a.</i>	3.12
Perfluoroheptanoic acid (PFHpA)	364	CF ₃ (CF ₂) ₅ COO ⁻	375-85-9	118 (24°C)	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	175 (742 mm Hg)	128	<i>n.a.</i>	4.59
Perfluorooctanoic acid (PFOA)	414	CF ₃ (CF ₂) ₆ COO ⁻	335-67-1	4.3 (24°C)	2.5	2.6	45-50	189-192 (736 mm Hg)	70	<i>n.a.</i>	<i>n.a.</i>
Perfluorononanoic acid (PFNA)	464	CF ₃ (CF ₂) ₇ COO ⁻	375-95-1	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	67-70	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>
Perfluorodecanoic acid (PFDA)	514	CF ₃ (CF ₂) ₈ COO ⁻	335-76-2	0.26 (24°C)	<i>n.a.</i>	<i>n.a.</i>	83-85	218 (740 mm Hg)	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>
Perfluoroundecanoic acid (PFUnA)	564	CF ₃ (CF ₂) ₉ COO ⁻	2058-94-8	0.092 (24°C)	<i>n.a.</i>	<i>n.a.</i>	96-101	160 (60 mm Hg)	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>
Perfluorododecanoic acid (PFDoA)	614	CF ₃ (CF ₂) ₁₀ COO ⁻	307-55-1	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	107-109	245 (740 mm Hg)	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>
2-Perfluorohexyl ethyl alcohol (6:2 FTOH)	364	CF ₃ (CF ₂) ₅ (CH ₂) ₂ OH	647-42-7	0.019 (22°C)	<i>n.a.</i>	3-7 (20°C)	-35	70 (20 mm Hg)	713	3.6-5.3 (25°C)	4.54
2-Perfluorooctyl ethyl alcohol (8:2 FTOH)	464	CF ₃ (CF ₂) ₇ (CH ₂) ₂ OH	678-39-7	1.1x10 ⁻⁵ (22°C)	<i>n.a.</i>	<i>n.a.</i>	47	113 (10 mm Hg)	254	4.2-5.6 (25°C)	5.58
2-Perfluorodecyl ethyl alcohol (10:2 FTOH)	564	CF ₃ (CF ₂) ₉ (CH ₂) ₂ OH	865-86-1	6.0x10 ⁻⁶ - 8.9x10 ⁻⁴ (22°C)	<i>n.a.</i>	<i>n.a.</i>	95	145 (10 mm Hg)	144	4.8-5.5 (25°C)	6.63

Source: Danish EPA, 2008; Carmosini and Lee, 2008; Kunacheva, 2009; Deng *et al.*, 2012Note: *n.a.* = not available

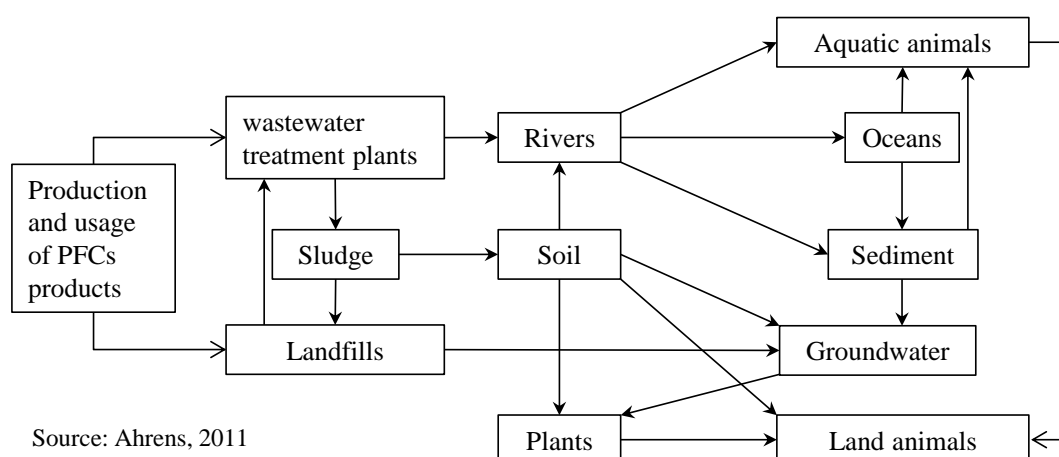


Figure 2.1 Contamination pathways of PFCs in environment

FTOHs are thought to be emitted to the atmosphere during their production and more importantly by diffuse sources during use and disposal (Dreyer *et al.*, 2009a). FTOHs are recognized as the indirect sources of PFCAs in remote areas due to their volatile and degradable properties. Recently, FTOHs were detected in air environment was reported in several developed countries, including in the atmosphere above the Arctic, Atlantic and Southern Oceans. Therefore, not only aquatic environment but also atmosphere is needed to be concerned for contamination pathways of PFCAs and FTOHs in the environment.

2.2 FTOHs and PFCAs in Air Environment

2.2.1 Occurrence and Levels

FTOHs *i.e.* 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were widely detected in outdoor air in several countries in North America, Europe and Asia (Stock *et al.*, 2004; Jahnke *et al.*, 2007a; Barber *et al.*, 2007; Oono *et al.*, 2008a; Oono *et al.*, 2008b; Vierke *et al.*, 2011; Shoeib *et al.*, 2011; Kim *et al.*, 2012), as well as along the Arctic, Atlantic and Southern oceans (Shoeib *et al.*, 2006; Jahnke *et al.*, 2007b; Dreyer and Ebinghaus, 2009; Dreyer *et al.*, 2009a; Shoeib *et al.*, 2010; Cai *et al.*, 2012), which showed evidences of their global atmospheric distribution.

At present, several data sets of FTOHs concentrations in developed countries are available for outdoor and indoor air samples (**Appendix A**). In outdoor air, total concentrations of 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were in the range of 10-20,000 pg/m^3 (**Fig. 2.2**). Lower concentrations of FTOHs were detected for ship-based sites compared to land-based sites (Dreyer and Ebinghaus, 2009). FTOHs were measured in ambient air on a cruise transect from the Japan Sea to the Arctic Ocean and air mass back trajectories were used to determine the source routes of FTOHs (Cai *et al.*, 2012). This previous study indicated that much higher concentrations would be expected if the air had come directly from Asian countries. In Asian countries, FTOHs in air were detected only in Japan (Oono *et al.*, 2008a; Oono *et al.*, 2008b) and Korea (Kim *et al.*, 2012) and the concentrations were higher than those in Europe and North America countries. These results suggested an Asian origin of FTOHs. However, limited measurements of airborne FTOHs were conducted in the other parts of Asian countries, especially in developing countries with industrialization but without strict environmental regulations.

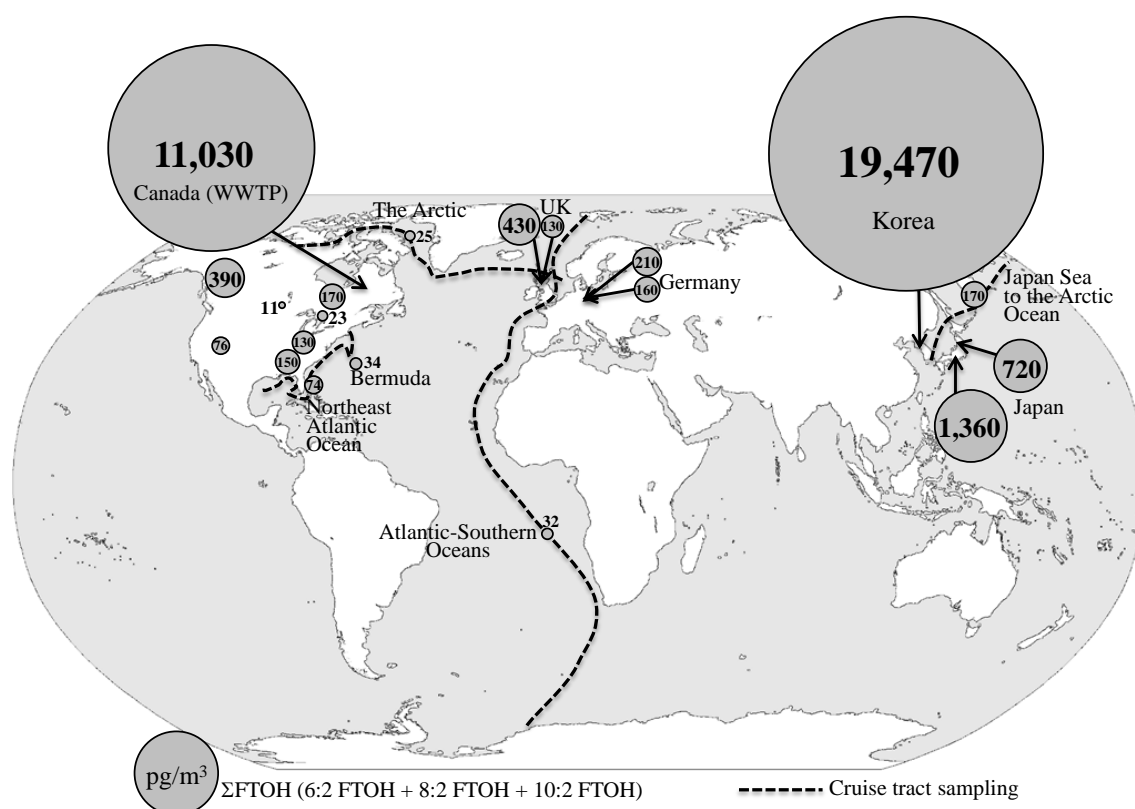


Figure 2.2 Occurrences of FTOHs in outdoor air in previous studies

The highest concentration of FTOHs was detected at industrial areas in Korea, which suggested industrial activities as the potential sources of FTOHs. High concentrations of FTOHs were also observed in urban areas and traffic-influenced areas (Stock *et al.*, 2004; Harada *et al.*, 2005; Jahnke *et al.*, 2007a). These results showed that high density and activities of populated areas could also be a significant source of FTOHs emission to atmosphere.

Compared to outdoor air, higher concentrations of FTOHs were detected in indoor air such as in house, office, printing shop and furniture shop, *etc.* (Appendix A). Concentrations of FTOHs were in the range of 5,000-130,000 pg/m³ in indoor air (Fig. 2.3). High FTOHs concentrations in indoor air indicated their possible indoor sources, which were reported by previous studies (Barber *et al.*, 2007; Langer *et al.*, 2010; Shoeib *et al.*, 2011). FTOHs are used as surfactants in several products such as carpet, textile, paper, paints, coatings and adhesives, and there is potential for residual FTOHs (unreacted and unbound) to be released from these products (Dinglasan and Mabury, 2006).

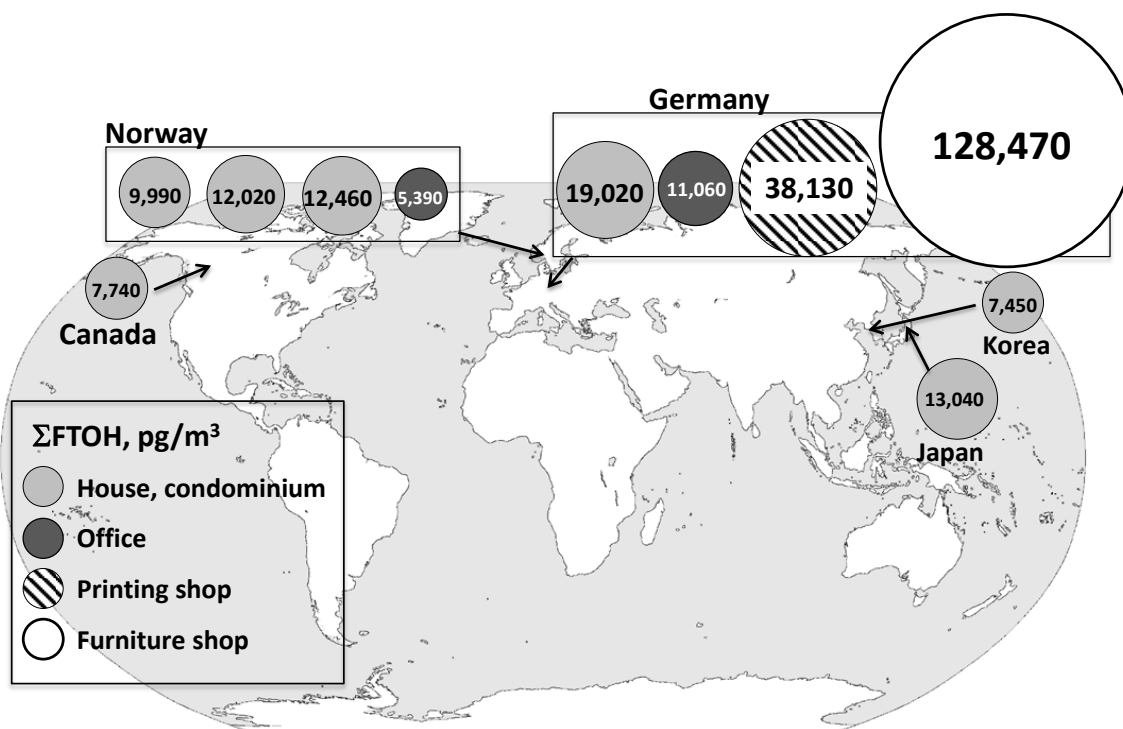


Figure 2.3 Occurrences of FTOHs in indoor air in previous studies

PFCAs were also detected in air by mostly bound with particulate matter. The concentrations in outdoor and indoor air ranged between 2-380 pg/m³ (**Appendix A**). Only a few studies have reported their presence in the gas-phase. Being dissolved in the water phase or enriched at the water surface, PFCAs may also be transported into the air as marine aerosols (Prevedouros *et al.*, 2006; Dreyer *et al.*, 2009a). Vierke *et al.* (2011) have shown the presence of PFCAs in gas-phase with the range between 0.004-50 pg/m³ at an aeration tank of a wastewater treatment plant (WWTP). WWTPs are suggested as potential point sources of FTOHs and PFCAs to atmosphere. Water to air transport of these compounds is believed to be enhanced at the aeration tank owing to aerosol-mediated transport caused by surface turbulence induced by aeration (Vierke *et al.*, 2011).

2.2.2 Sampling and Analytical Methods

There are several challenges for determination of FTOHs and PFCAs in air such as low concentration levels, sampling and analytical procedures, matrix enhancement and contamination (Huber *et al.*, 2011; Ahrens, 2011). Reviews of analytical procedures of FTOHs and PFCAs in air samples in previous studies are detailed in **Appendix B** and summarized in **Fig. 2.4**. Two types of air sampling method (*i.e.* active and passive) were applied to collect the air. Active air sampling with high volume air sampler (100-700 L/min) was mostly used for outdoor sites, whereas the low volume air sampler (0.004-2 L/min) and passive air sampling were applied for indoor sites. Two types of sampling media *i.e.* glass fiber filters (GFFs) and quartz fiber filters (QFFs) were used to collect particle-phase FTOHs and PFCAs. For the gas-phase fractions, XAD-2 resin or activated carbon fiber (ACF) sandwiched by polyurethane foam (PUF/XAD-2/PUF or PUF/ACF/PUF) were used. Sorbent-impregnated polyurethane foam (SIP) disk was normally applied as sampling media to collect both particle and gas-phase of FTOHs and PFCAs for passive air sampling method.

There are three main steps for air sample preparation including extraction, concentration and clean-up. Several types of extraction method were developed for FTOHs and PFCAs analysis such as Soxhlet apparatus extraction, sonication, soaking and shaking, fluidized bed extraction, cold column extraction and accelerated solvent extraction.

Several organic solvents were used for the extraction of FTOHs and PFCAs such as methanol, ethyl acetate, dichloromethane, acetone, petroleum ether, methyl tetra butyl ether (MTBE) and hexane. Second step of sample preparation, the extract was concentrated using high efficiency evaporator (*i.e.* Rotary, RapidVap, TurboVap) and blowing with nitrogen gas. The last step was clean-up of concentrated samples. Chemical dry using sodium sulfate, silica gel or alumina gel was conducted to remove water for FTOHs samples, and Envi-carb cartridges were used for matrix removal for PFCAs samples.

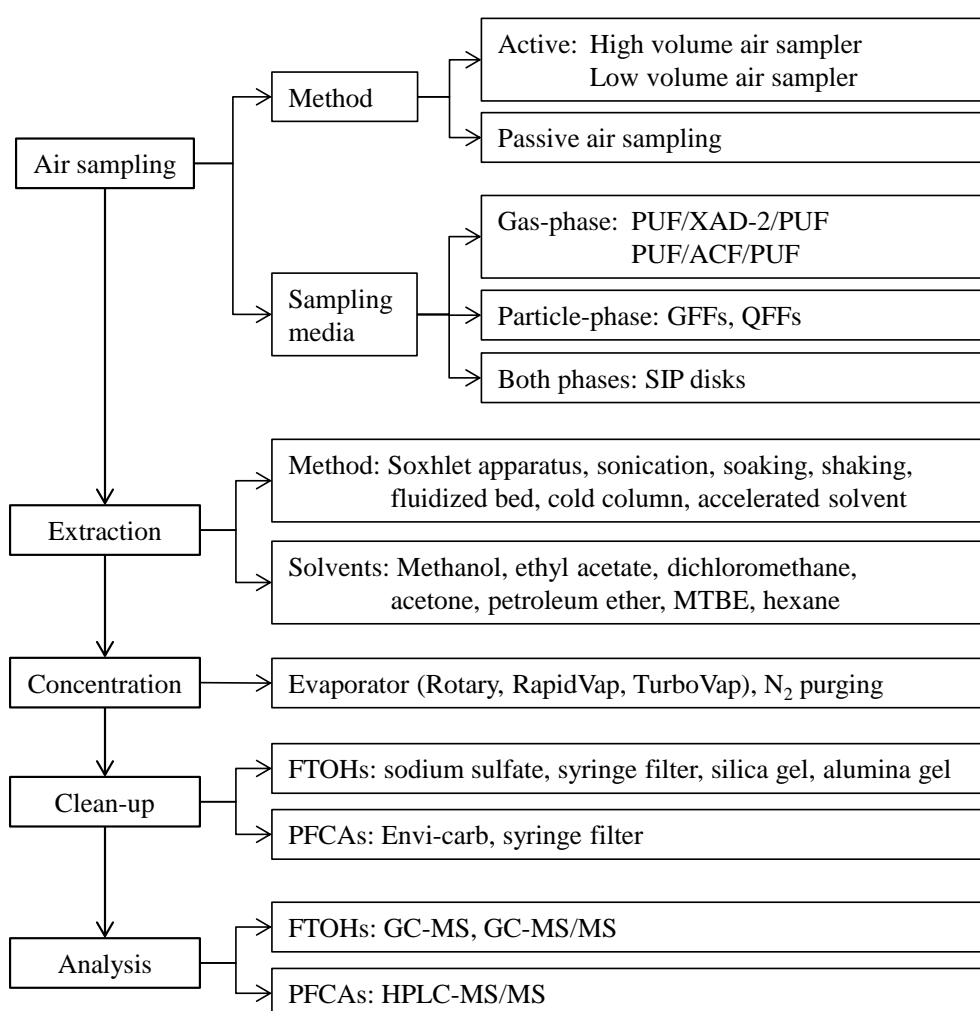


Figure 2.4 Reviews of sampling and analytical methods for FTOHs and PFCAs in air samples

For analysis step, FTOHs were normally analyzed by gas chromatography couple with mass spectrometer (GC-MS), whereas the high efficiency detector instrument *i.e.* triple quadrupole mass spectrometer (GC-MS/MS) was rarely applied. PFCAs were mostly analyzed using high performance liquid chromatography couple with triple quadrupole mass spectrometer (HPLC-MS/MS).

2.2.3 Atmospheric Fate and Lifetime

Atmospheric removal mechanism for PFCAs is suggested to be wet and dry deposition which can occur on a time scale of 10 days (Hurley *et al.*, 2004). Due to their low volatility and efficient scavenging by wet deposition, PFCA are unlikely to travel long distances in the atmosphere (Dreyer and Ebinghaus, 2009). On the other hand, relatively high vapor pressure and low water solubility of FTOHs are likely to deter their wet deposition from the atmosphere (Ellis *et al.*, 2003; Loewen *et al.*, 2005). In the atmosphere, hydroxyl (OH) radical initiated oxidation appears to be a degradation route of FTOHs. Smog chamber studies of FTOHs showed that corresponding or shorter chain length PFCAs were formed and atmospheric lifetime of FTOHs was estimated to be 20 days based on reaction with OH radical (Ellis *et al.*, 2003). Field studies estimated atmospheric lifetime of 50-80 days for FTOHs (Piekarz *et al.*, 2007). These data indicated the possibility of regional and long-range atmospheric transport of FTOHs.

2.3 Wet Deposition Process of PFCAs and FTOHs

Wet deposition was suggested as an effective atmospheric removal and one of the contamination sources of PFCAs in river water (Kwok *et al.*, 2010; Taniyasu *et al.*, 2013a). PFCAs were detected in rainwater in several countries such as USA, Germany, France, India, China and Japan (Kim and Kannan, 2007; Liu *et al.*, 2009; Dreyer *et al.*, 2010; Kwok *et al.*, 2010). The concentrations of PFCAs in these previous studies ranged between 1-50 ng/L (**Fig. 2.5**). Differences in concentrations and composition profiles of PFCAs among regions may reflect local atmospheric contamination (Kwok *et al.*, 2010). Very few studies have been conducted FTOHs measurements in aqueous samples. The first study to quantify FTOHs in rainwater was conducted in Kyoto, Japan

(Mahmoud *et al.*, 2009). The concentration of 8:2 FTOH and 10:2 FTOH during 3 rain events ranged between 1.01-3.18 ng/L and <0.2-1.28 ng/L, respectively.

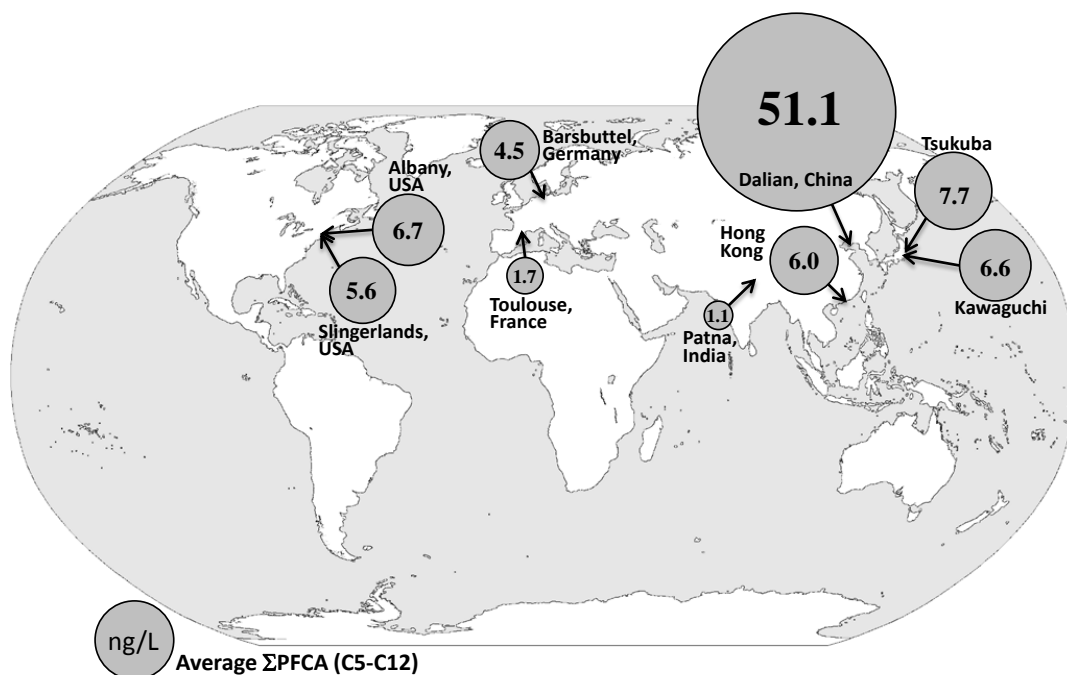


Figure 2.5 Occurrence of PFCAs in rainwater samples in previous studies

2.4 Photodegradability of PFCAs and FTOHs

Due to the strength of the carbon-fluorine bonds ($>450 \text{ kJ mol}^{-1}$) (Ahrens, 2011), PFCAs are persistent to acids, bases, oxidants, and reductants and are generally not believed to undergo environmental degradation (Prevedouros, 2006). Photolysis half-life of PFOA in water environment was estimated as 349 days (Environment Canada, 2010). Most of photolysis research of PFOA has focused on UV-C irradiation (100 nm to 280 nm) and advanced oxidation for wastewater treatment purposes (**Table 2.3**). The first study of photodegradation of PFCAs under natural environmental conditions was conducted by Taniyasu *et al.* (2013). PFCAs solutions were exposed to sunlight at high altitude mountains and their concentrations decreased which suggested that PFCAs can undergo photodegradation in the environment.

Table 2.3 Summary for photodegradation of PFCAs and FTOHs by previous studies

Studies	Light	Compounds	Initial conc.	Time (hr)	Degradation rates	Catalysts/ sensitizers
Hori et al.(2005)	UV (220-460 nm)	PFPeA	1.33 mM	12	98.6%	S ₂ O ₈ ²⁻ (50 mM)
		PFHxA	1.34 mM	12	100%	S ₂ O ₈ ²⁻ (50 mM)
		PFOA	1.35 mM	4	100%	S ₂ O ₈ ²⁻ (50 mM)
		PFHpA	1.33 mM	12	100%	S ₂ O ₈ ²⁻ (50 mM)
		PFNA	0.67 mM	12	100%	S ₂ O ₈ ²⁻ (50 mM)
Chen <i>et al.</i> (2007)	UV (254 nm)	PFOA	0.06 mM	2	~5%	-
	UV (185 nm)	PFOA	0.06 mM	2	61.7%	-
Wang <i>et al.</i> (2008)	UV (254 nm)	PFOA	48 µM	4	47.3%	Fe ³⁺ (10 mM)
		PFOA	48 µM	4	80.2%	Fe ³⁺ (80 mM)
Estrellan <i>et al.</i> (2010)	UV (200-600 nm)	PFOA	0.1 mM	3	~15%	Fe&Nb co-doped TiO ₂ (0.5 g/L)
		PFOA	0.1 mM	3	~7%	pure TiO ₂ (0.5 g/L)
Vaalgamaa <i>et al.</i> (2011)	UV (254 nm)	PFOA	100 ng/L	144	28%	Fe ³⁺ (2.79 mg/L)
		PFOA	100 ng/L	144	26%	NO ₃ ²⁻ (1 mg/L)
		PFOA	100 ng/L	144	31%	Fulvic acid (15 mgC /L)
		PFOA	100 ng/L	144	45%	Sea water
		PFOA	100 ng/L	144	24%	<i>MiliiQ</i>
	Artificial sun (290-800 nm)	PFOA	100 ng/L	165	0%	Fe ³⁺ / NO ₃ ²⁻ / Fulvic acid
Taniyasu <i>et al.</i> (2013)	Solar radiation at high mountain	PFOA	2.55 µM	1,232	5%	-
		PFNA	1.80 µM	1,232	19%	-
		PFDA	1.08 µM	1,232	35%	-
		6:2 FTOH	24.7 µM	1,232	75%	-
		8:2 FTOH	8.38 µM	1,232	90%	-
	UV	PFOA	0.45 µM	216	31%	-
		PFDA	0.39 µM	216	61%	-
		8:2 FTOH	185 µM	216	99%	-
Gauthier and Mabury (2005)	Artificial sun (290-800 nm)	8:2 FTOH	50 µg/L	0.83	50%	H ₂ O ₂ (10 mM)
		8:2 FTOH	50 µg/L	38	50%	H ₂ O ₂ (100 µM)

Precursor compounds play an important role as the potential sources of PFCAs in the environment. Being in aqueous environments, they may degrade *via* several routes such as hydrolysis, microbial degradation and photodegradation (Gauthier and Mabury, 2005). Solar radiation induced photolysis is the primary route for degradation of many anthropogenic chemicals (Vaalgamaa *et al.*, 2011). FTOHs are less persistent than PFCAs and they can be degraded in environmental conditions. Degradation of 8:2 FTOH in water environment was observed by biological and photolysis processes. Half-life of 8:2 FTOH by aerobic biodegradation using a mix microbial system was estimated as 4.4 hours (Dinglasan *et al.*, 2004) and was 0.83 hours by indirect photolysis (irradiated in a suntest photosimulator) using hydroxyl radicals (10 mM hydrogen peroxide solution) as the main degradation agent (Gauthier and Mabury, 2005). Degradation of 6:2 FTOH and 8:2 FTOH was observed by solar radiation and UV light, and the degradation rates were between 75-99% (Taniyasu *et al.*, 2013).

2.5 Human Risk Assessment of PFCAs and FTOHs

2.5.1 Toxicity

PFOA were detected in adult populations in many countries worldwide, including United States, Canada, Italy, Poland, Belgium, Sweden, Germany, Spain, Australia, Columbia, Brazil, India, Malaysia, Korea, Japan and China (Lau *et al.*, 2007). Other PFCAs such as PFPeA, PFHxA, PFHpA, PFNA, PFDA and PFUnDA were also detected in human tissue (Lau *et al.*, 2007). The mean half-life of PFOA in human blood was estimated to be 3.8 years (Olsen *et al.*, 2007) and the renal clearances of PFOA are almost negligible in human (Harada *et al.*, 2005). Therefore, PFOA may be accumulated in internal organs such as livers and kidney (Danish EPA, 2008). In human, inverse association between PFOA concentrations in maternal cord serum/plasma and birth weight were observed (Apelberg *et al.*, 2007; Fei *et al.*, 2007). Other toxicities and health effects of PFCAs and FTOHs have been not reported in human. However, several toxicities were observed in laboratory animal tests including hepatotoxicity, developmental toxicity, immunotoxicity, reproduction toxicity, endocrine toxicity (hormone effects), and death (Lau *et al.*, 2007; Andersen *et al.*, 2008).

2.5.2 Human Exposure Assessment

Several experimental studies have demonstrated toxic effects of PFCAs in animal tests and PFCAs were detected in human blood worldwide but the sources and pathways of exposure remain unclear. Most of the previous results (**Table 2.4**) showed that dietary and drinking water consumption were important pathways of exposure to PFCAs (Bjorklund *et al.*, 2009; Fromme *et al.*, 2009; Kim *et al.*, 2012; Jogsten *et al.*, 2012). Few studies reported that dust consumption was found to be a significant pathway of exposure to PFCAs, especially for toddler (Strynar and Lindstrom, 2008; Shoeib, *et al.*, 2011). However, studies on human exposure to PFCA's precursors have been limited. Air inhalation was reported to be an important pathway of exposure to FTOHs (Haug *et al.*, 2011; Shoeib, *et al.*, 2011) and this contribution might be a significant pathway for PFCAs exposure. Calculation of daily intakes of PFCAs and FTOHs in mentioned studies and related parameters are detailed in **Appendix C**.

Formation of PFCAs by metabolisms of FTOHs were investigated in vivo experiments (*e.g.* mice, rat, etc.), and vitro experiments (*e.g.* hepatocytes, microsomes and cytosol). Even though, metabolic transformation is different among species, exposure to FTOHs might be sources of PFCAs in human (Kudo *et al.*, 2005; Martin *et al.*, 2005; Fasano *et al.*, 2006; Nabb *et al.*, 2007; Henderson and Smith, 2007).

2.5.3 Guidelines and Acceptable Levels

At present, only guidelines and acceptable levels of PFOA are available among PFCAs and FTOHs (**Table 2.5**). Guideline for PFOA concentration levels in drinking water was set between 0.04-10 µg/L. The U.K. Committee on Toxicology (2006) has recommended a Tolerable Daily Intake (TDI) for PFOA at 3 µg/kg bw/day, while Japan government has recommended a strict TDI for PFOA at 0.3 µg/kg bw/day.

Table 2.4 Summary of average daily intake of PFCAs and FTOHs in previous studies

Locations	Pathways	Pollutants	Intake (ng/kg-day)	
			Adult	Children
Sweden	Dust ingestion	PFOA	0.005 ^a	0.200 ^a
(Bjorklund <i>et al.</i> , 2009)	Food consumption	PFOA	1.167 ^a	0.015 ^a
European Country	Air inhalation	PFOA	0.002	-
(Fromme <i>et al.</i> , 2009)	Dust ingestion	PFOA	0.016	-
	Food consumption	PFOA	2.817	-
	Drinking water	PFOA	0.022	-
Norway	Air inhalation	PFOA	0.013	0.047
(Haug <i>et al.</i> , 2011)	Dust ingestion	PFOA	0.032	0.390
	Food consumption	PFOA	0.240	13.0
	Drinking water	PFOA	0.031	
Canada	Air inhalation	FTOHs+FOSA+FOSE	0.714 ^a	2.067 ^a
(Shoeib <i>et al.</i> , 2011)		PFCAs+PFOS	0.045 ^a	0.120 ^a
	Dust ingestion	FTOHs+FOSA+FOSE	0.005 ^a	0.507 ^a
		PFCAs+PFOS	0.012 ^a	1.133 ^a
Spain	Air inhalation	FTOHs	0.019	0.050
(Jogsten <i>et al.</i> , 2012;		PFCAs+PFSA+FTUCA	0.039	0.100
Domingo <i>et al.</i> , 2011)		PFOA	0.008	0.023
	Dust ingestion	FTOHs	3.7x10 ⁻⁴	0.002
		PFCAs+PFSA+FTUCA	0.051	0.327
		PFOA	0.007	0.043
	Food consumption	PFOA	0.340	-
	Drinking water	PFOA	0.070	-
Korea	Air inhalation	FTOHs	4.20	-
(Kim <i>et al.</i> , 2012)				

Note: ^a Adapted based on adult 60 kg and children 15 kg, FOSAs = perfluorooctane sulfonamide, FOSE = perfluorooctane sulfonamidoethanol, FTUCAs = fluorotelomer unsaturated acids

Table 2.5 Guidelines and acceptance levels for PFOA

Guideline	Levels	Country/ organization	References
Drinking water	0.04 µg/L	New Jersey	Maxxam Analytics International Corporation (2012)
	0.3 µg/L	Minnesota	
	0.4 µg/L	US.EPA.	
	0.7 µg/L	Canada	
	2 µg/L	North Carolina	
	10 µg/L	UK. HPA.	
Tolerable	3 µg/kg bw/day	U.K.	UK Food Standards Agency (2006)
daily intake	0.3 µg/kg bw/day	Japan	Japan government (2008)

Chapter 3

Contamination of FTOHs and PFCAs in Air Environment in Thailand

3.1 Introduction

Several monitoring studies have demonstrated contamination of PFCAs in aquatic environment which is believed to be main transport pathways and ultimate sinks of PFCAs (Fujii *et al.*, 2007; Lau *et al.*, 2007; Ahrens, 2011). However, their detection in remote areas raise concerns about atmospheric contamination pathways, which currently limited data is available.

PFCAs are not found in significant quantities as a vapor (Barton *et al.*, 2007) but they can be associated with particulate matter in the air. In addition, their volatile precursor compounds *i.e.* FTOHs are suggested as indirect sources of PFCAs in the environment. In recent years, FTOHs were widely detected in the air not only in developed countries but also along the Arctic, Atlantic and Southern oceans, which showed evidences of global atmospheric distribution (Dreyer *et al.*, 2009a). Information on contamination of FTOHs and PFCAs in air environment has been developed, but it is mainly in developed countries while very few studies have been conducted in developing countries.

In Thailand, PFCAs were detected in surface water (*i.e.* rivers, reservoirs and coastal water), industrial and domestic wastewater, food and house dust (Kunacheva *et al.*, 2009; Chularueangaksorn *et al.*, 2012; Haruka *et al.*, 2012; Goosey and Harrad, 2011). However, contamination of PFCAs and their precursor compounds (*i.e.* FTOHs) in air in Thailand have not been studied. Investigation of FTOHs and PFCAs in air environment of developing countries like Thailand could provide important information to understand their worldwide contamination. The information could also explain their distribution and behaviors in air in Thailand and human exposure to these compounds by inhalation pathways.

3.2 Objectives

The purposes of this field study were (1) to investigate contamination of FTOHs and PFCAs in various outdoor and indoor air sampling sites in Thailand, (2) to compare their concentration levels among the sampling sites and with the levels in other countries, (3) to investigate temporal variation and their possible sources to the air, (4) to examine their behaviors and factors influencing their occurrence in the air, and (5) to calculate intakes of FTOHs and PFCAs by inhalation exposure pathways and compare the exposure levels with other pathways.

3.3 Methodology

3.3.1 Sampling Locations

First survey was conducted in the Central and Eastern parts of Thailand during September 10 to October 29, 2012. Various outdoor and indoor areas (**Fig 3.1**), which are suspected to be contaminated by FTOHs and PFCAs, were selected as air sampling sites. Detailed characteristics of the sites; wastewater treatment plants (WWTPs) and residential areas for outdoor air, and the places for indoor air, are demonstrated in **Table 3.1**.

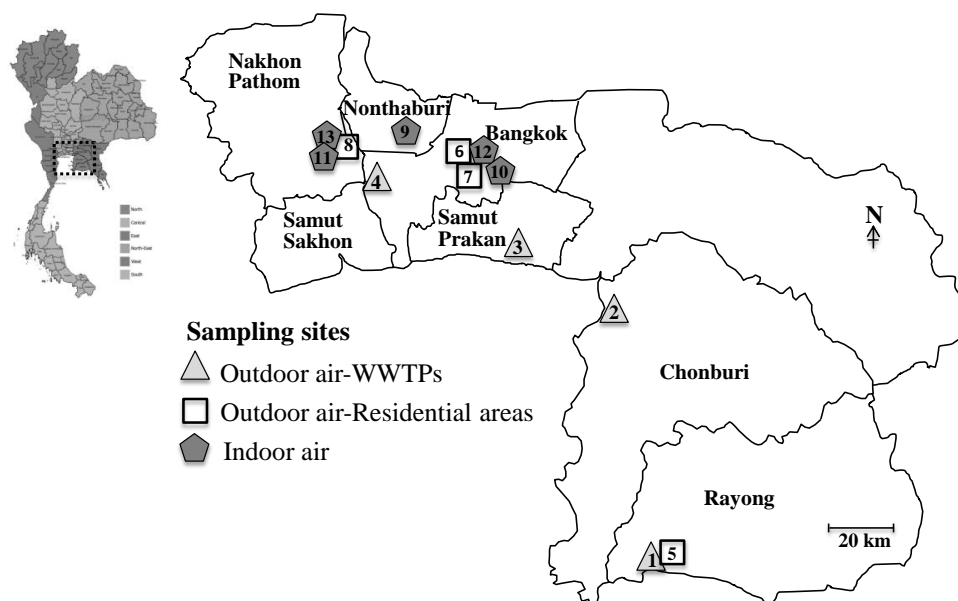


Figure 3.1 Outdoor and indoor air sampling sites in Thailand

Table 3.1 Locations and characteristics of air sampling sites in Thailand

Sampling sites		Locations	Site characteristics		
Outdoor air-wastewater treatment plants (WWTPs)			Capacity (m ³ /day)	No. of industries	Main industrial types
1	Industrial WWTP1	Industrial estate1 (IE1), at aeration tank	4,000	213	- Chemical and related (55.4%) - Petroleum and energy (19.2%) - Plastic (7.0%)
2	Industrial WWTP2	Industrial estate2, at aeration tank	16,000	244	- Automotive (32.9%) - Steel and metal (17.5%) - Electronics and electrical (14.0%)
3	Industrial WWTP3	Industrial estate3, at aeration tank	45,000	350	- Steel and metal (15.0%) - Paper and printing (13.0%) - Chemical and related (12.0%)
4	Domestic WWTP4	Suburban area, at aeration tank	157,000	Service area 44 km ² ; 418,000 people	
Outdoor air-residential areas (RA)			No. of households	Population density (capita/km ²)	Characteristics
5	RA1	Industrial area	42,295	390	Northeast, 5 km from IE1
6	RA2	Urban area (roadside area)	51,686	16,098	~10 m from traffic lanes of the main road
7	RA3	Urban area	55,575	6,441	~1 km from the main road
8	RA4	Suburban area	14,568	640	At a university
Indoor air			Room size (m ²)	Ventilation systems	Activities/ characteristics
9	Condominium	Suburban area	30	Air conditioning	Recently built, painted and decorated (new furniture and carpets)
10	Printing shop	Urban area	48	Air conditioning	Document and poster printing
11	Office1	Suburban area	12	Air conditioning	Instructor's room in a university, re-painted room
12	Office2	Urban area	225	Air conditioning	Document and report preparing
13	Laboratory	Suburban area	74	Air conditioning and exhaust fan	Water analysis laboratory in a university
14	Furniture shop	Suburban area	150	No air conditioning	Wood furniture, natural wind through opened door, window and porous wall

To study temporal variation of target compounds, second survey was conducted for seven consecutive days of monitoring at selected three sampling sites; industrial WWTP (WWTP1; January 10-17, 2013), industrial area (RA1; January 2-9, 2013) and urban area (RA2; December 24-30, 2012).

3.3.2 Chemicals and Standards

Eleven target compounds of three FTOHs (*i.e.* 6:2 FTOH, 8:2 FTOH and 10:2 FTOH), and eight PFCAs (*i.e.* PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDODA), and an internal standard (8:1 FA) were purchased from Wako Pure Chemicals (Osaka, Japan). Four mass-labeled standards ($^{13}\text{C}_2$ 8:2 FTOH, $^{13}\text{C}_2$ -PFHxA, $^{13}\text{C}_4$ -PFOA and $^{13}\text{C}_2$ -PFDA) were purchased from the Wellington Laboratory Inc. (Ontario, Canada). Chemicals and standards of FTOHs and PFCAs which were used in this study are shown in **Table 3.2**. Analytical or HPLC grade were used for all solvents and reagents.

Table 3.2 Details of chemicals and standards in this study

Compounds	Abbreviation	Supplier
<u>Target fluorotelomer alcohols (FTOHs)</u>		
6:2 Fluorotelomer alcohol	6:2 FTOH	Wako Pure Chemicals
8:2 Fluorotelomer alcohol	8:2 FTOH	Wako Pure Chemicals
10:2 Fluorotelomer alcohol	10:2 FTOH	Wako Pure Chemicals
<u>Target perfluoroalkyl carboxylates (PFCAs)</u>		
Perfluoropentanoic acid	PFPeA	Wako Pure Chemicals
Perfluorohexanoic acid	PFHxA	Wako Pure Chemicals
Perfluoroheptanoic acid	PFHpA	Wako Pure Chemicals
Perfluorooctanoic acid	PFOA	Wako Pure Chemicals
Perfluorononanoic acid	PFNA	Wako Pure Chemicals
Perfluorodecanoic acid	PFDA	Wako Pure Chemicals
Perfluoroundecanoic acid	PFUnDA	Wako Pure Chemicals
Perfluorododecanoic acid	PFDODA	Wako Pure Chemicals
<u>Internal standard</u>		
1H,1H-Perfluoro-1-nanol	8:1 FA	Wako Pure Chemicals
<u>Mass labeled standards</u>		
2-Perfluorooctyl-[1,1- $^2\text{H}_2$]-[1,2- $^{13}\text{C}_2$]-ethanol	$^{13}\text{C}_2$ -8:2 FTOH	Wellington Laboratory Inc.
Perfluoro-n-[1,2- $^{13}\text{C}_2$] hexanoic acid	$^{13}\text{C}_2$ -PFHxA	Wellington Laboratory Inc.
Perfluoro-n-[1,2,3,4- $^{13}\text{C}_4$] octanoic acid	$^{13}\text{C}_4$ -PFOA	Wellington Laboratory Inc.
Perfluoro-n-[1,2- $^{13}\text{C}_2$] decanoic acid	$^{13}\text{C}_2$ -PFDA	Wellington Laboratory Inc.

3.3.3 Sample Collection

Air samples were collected using a high volume air sampler (HV-500F, Sibata, Saitama, Japan) at a flow rate of 500 L/min for 24 hours (about 720 m³). This study adapted three types of media for air sampling; glass fiber filters (GFFs, GB100R grade, ϕ 110 mm, 0.6 μ m pore size, Advantec®, Toyo Roshi Kaisha, Ltd., Tokyo, Japan), polyurethane foams (PUFs, ϕ 90 \times 50 mm, Sibata, Saitama, Japan) and activated carbon fiber felts (ACFs, ϕ 84 \times 2 mm, Sibata, Saitama, Japan).

All of these sampling media were pre-cleaned by soaking them twice in ethyl acetate, followed by 3 times in methanol. Soaking time was 1 hour for every process. PUFs and ACFs were dried overnight at 60 °C in a drier while GFFs were heated at 250°C for 2 hours in an oven. Pre-cleaned media were wrapped in aluminum foil and sealed in zip lock polypropylene (PP) plastic bags for transportation to the sampling sites.

One set of the sampling media (GFF and PUF/ACF/PUF) was used to collect the target compounds at each sampling site. Particle-phase fraction of the target compounds was collected on a GFF, while gas-phase fraction was trapped in a column of PUF/ACF/PUF. After sampling, these sampling media (air samples) were wrapped in aluminum foil, sealed in zip lock PP plastic bags and stored at 4°C until analysis.

Another set of the media was also prepared as a field blank to examine contamination during all of the procedures. The field blank set was handled with a completely same procedure as that for the sample set except that it was just placed close to the sampling points without installation in the vacuum pump for sampling. For first survey, the field blank tests were conducted at four sampling sites of two industrial WWTPs (industrial sources), an urban area (most populated area) and a condominium (recently built, painted and decorated). For second survey, one field blank was collected at each sampling site.

3.3.4 Sample Preparation

Each air sample was prepared for analysis of three portions; particle-phase FTOHs, gas-phase FTOHs and particle-phase PFCAs. For extraction of particle-phase FTOHs, a half of GFF was soaked in 10 mL methanol and shaken at 150 rpm for 1 hour. The extraction process was repeated for 4 times (about 40 mL of extracts in total). For gas-phase FTOHs extraction, PUFs were soaked in 250 mL methanol and shaken at 150 rpm for 1 hour. Then, they were soaked in 150 mL methanol for three more times (about 700 mL of extracts in total). ACF was soaked in 50 mL methanol and shaken at 150 rpm for 1 hour, and the extraction was done for 4 times (about 200 mL of extracts in total). Finally, both extracts were combined to make 900 mL of a gas-phase extract. Mass-labeled FTOH ($^{13}\text{C}_2$ 8:2 FTOH) was spiked into the sampling media before extraction to confirm the recovery. Extracts of particle and gas-phase FTOHs were separately evaporated to 3-5 mL using a rotary evaporator. After that, the concentrated solutes were cleaned up using 0.2 μm syringe filters and chemically dried using sodium sulfate (Na_2SO_4) cartridges. The purified liquid extracts were concentrated to 1 mL under a gentle stream of nitrogen gas. 8:1 FA was added as an internal standard just prior to GC-MS analysis to correct sample volume variability.

The other half of GFF was used to determine particle-phase PFCAs. It was soaked in 10 mL methanol and shaken at 150 rpm for 1 hour. The extraction process was conducted for 4 times (about 40 mL of extracts in total). Mass-labeled PFCAs ($^{13}\text{C}_2$ -PFHxA, $^{13}\text{C}_4$ -PFOA and $^{13}\text{C}_2$ -PFDA) were spiked into the samples to calculate their recoveries. The extracts were passed through ENVI-carb filter (Sigma-Aldrich, Tokyo, Japan) to eliminate matrix. Then, the purified extracts were evaporated using nitrogen gas, and reconstituted into HPLC-MS/MS mobile phase (40% acetonitrile in *ultrapure* water) to 1 mL. Analytical procedures of FTOHs and PFCAs for air samples are shown in **Fig. 3.2**.

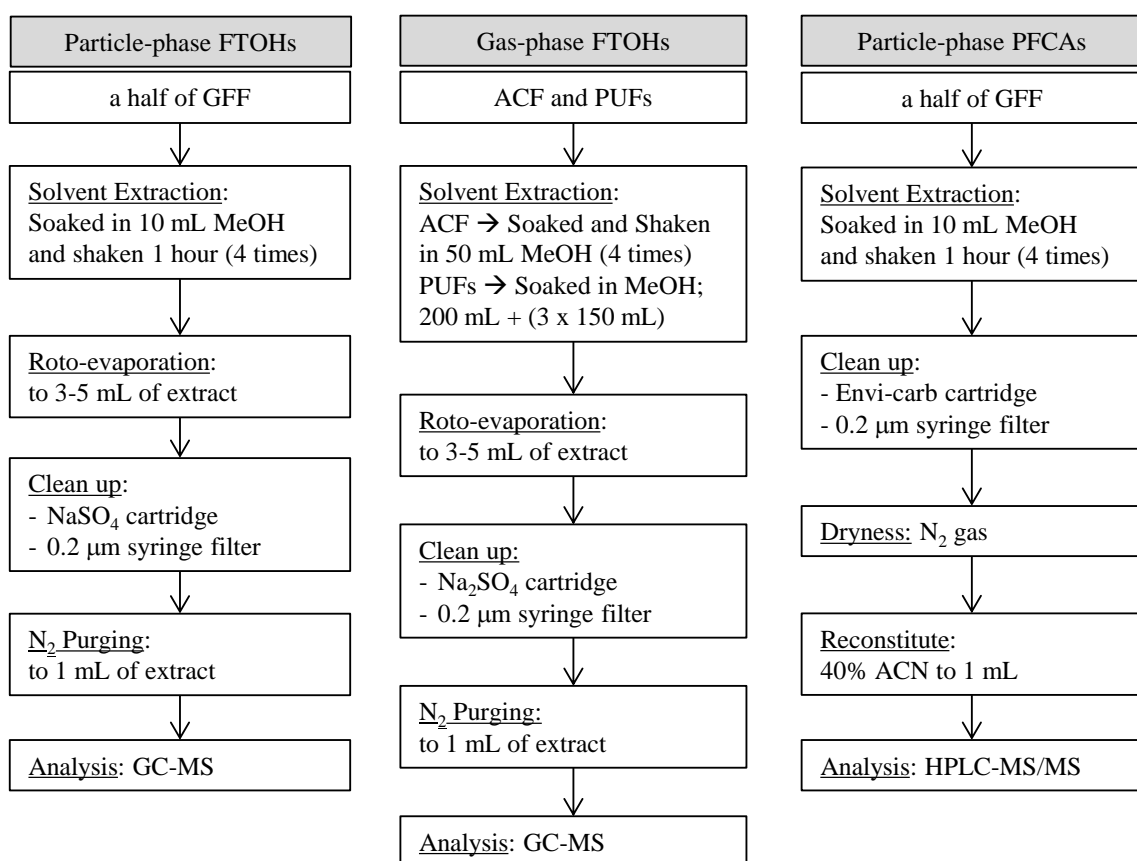


Figure 3.2 Analytical procedures of FTOHs and PFCAs for air samples in Thailand

3.3.5 Instrumental Analysis

FTOHs were analyzed by Agilent 6890 gas chromatography (GC)/Agilent 5973 mass spectrometer (MS) in electron ionization mode using selective ion monitoring (SIM). The purified extracts (2 µL) were injected to GC-MS with splitless mode at temperature of 230°C. The target compounds were separated on DB-WAX capillary column (30 m length with 0.25 mm inner diameter and 0.25 µm film thickness). Helium was employed as a carrier gas at a constant flow of 1 mL/min. GC oven was set at 50°C for 5 min, increased to 240°C with a ratio of 10°C/min (19 min) and hold at 240°C for 1 min, resulting in a run time of 25 min. Ion source and quadrupole temperatures were 230 °C and 150°C, respectively. **Table 3.3** shows analytical parameters of FTOHs *i.e.* quantifier and qualifier ions, and retention time (*RT*).

Table 3.3 Analytical parameters of FTOHs and PFCAs in air samples in Thailand

Compounds	Ion 1 (<i>m/z</i>)	Ion 2 (<i>m/z</i>)	<i>RT</i> (min)	<i>IDLs</i> (pg/ μ L)	<i>IQLs</i> (pg/ μ L)	<i>MDLs</i> (pg/m ³)	<i>SQLs</i> (pg/m ³)
<u>GC-MS</u>	<u>Quantifier ion</u>	<u>Qualifier ion</u>					
6:2 FTOH	95	31, 69, 131	9	7.4	24.6	10.3	34.2
8:2 FTOH	95	31, 69, 131	10.3	6.9	22.9	9.5	31.7
10:2 FTOH	95	31, 69, 131	11.7	8.1	27	11.2	37.5
8:1 FA	69	31, 95, 131	10.5	5.0	16.7	7.0	23.2
¹³ C ₂ -8:2 FTOH	131	31, 69, 95	10.3	12.3	41	17.1	57.0
<u>HPLC-MS/MS</u>	<u>Parent ion</u>	<u>Daughter ion</u>					
PFPeA	263	219	1.9	0.08	0.20	0.11	0.28
PFHxA	313	269	2.8	0.04	0.08	0.06	0.11
PFHpA	363	319	4.7	0.04	0.12	0.06	0.17
PFOA	413	369	7.2	0.04	0.12	0.06	0.17
PFNA	463	419	9.9	0.04	0.08	0.06	0.11
PFDA	513	469	12.7	0.04	0.16	0.06	0.22
PFUnDA	563	519	15.4	0.28	0.88	0.39	1.22
PFDoDA	613	569	18	0.28	0.88	0.39	1.22
¹³ C ₂ -PFHxA	315	271	2.8	0.04	0.08	0.06	0.11
¹³ C ₄ -PFOA	417	373	7.2	0.04	0.12	0.06	0.17
¹³ C ₂ -PFDA	515	471	12.7	0.04	0.12	0.06	0.17

PFCAs were analysed by Agilent 1200SL high performance liquid chromatography (HPLC) coupled with an Agilent 6400 Triple Quadrupole mass spectrometer (MS/MS) in electrospray ionization negative mode using multiple reactions monitoring. The purified extracts (10 μ L) were injected to Agilent Eclipse XDB-C18 column (inner diameter 2.1 mm, length 100 mm and particle size 5 μ m). Mobile phase consisted of (A) 5 mM ammonium acetate in *ultrapure* water and (B) 100% acetonitrile. At a flow rate of 0.25 mL/min, the separation process started with initial condition of 30% (B), increased to 50% (B) at 16.5 min, then to 70% (B) at 16.6 min and hold at 70% (B) for 3.4 min, after that went up to 90% (B) at 21 min and kept at 90% (B) for 1 min, and then ramped down to 30% (B), resulting a run time of 34 min. Table 3.3 also shows analytical parameters of PFCAs *i.e.* parent and daughter ions and retention time (*RT*).

3.3.6 Quality Assurance and Control (QA/QC)

The concentrations were calculated using five points standard curve analysis for FTOHs (10-1,000 pg/ μ L), and PFCAs (0.1-10 pg/ μ L), in which the determination coefficients (R^2) were more than 0.99. Instrument detection limit (*IDL*) was defined as concentrations with signal to noise ratio (*S/N*) equal to 3:1. Instrument quantification limit (*IQL*) was used for quantifying analytes, which were defined by *S/N* 10:1 (Oono et al., 2008a; Dreyer and Ebinghaus, 2009). Method detection limit (*MDL*) and method quantification limit (*MQL*) were calculated from the *IDL* and *IQL*, respectively, when 720 m³ of air sample was collected. *MDLs* of the target compounds were in the range of 0.06-11.2 pg/m³ (Table 3.3).

FTOHs and PFCAs in field blanks were below *MDLs*, indicating no contamination during the process. To correct sample volume variability, 8:1 FA was added as an internal standard just prior to GC-MS analysis. To confirm recovery of extraction and analysis method, mass-labeled standards were spiked to sampling media before extraction. The average recovery of ¹³C₂-8:2 FTOH was 96% and 98% for gas and particle-phase, respectively. For particle-phase of PFCAs, the average recovery of ¹³C₂-PFHxA, ¹³C₄-PFOA and ¹³C₂-PFDA were 90%, 96% and 104%, respectively (**Table 3.4**). Method recoveries for the analytical procedure are detailed in **Appendix D**.

Table 3.4 Recoveries of mass-labeled standard FTOHs and PFCAs

List	Gas-phase (<i>n</i> =10)	Particle-phase (<i>n</i> =10)			
	¹³ C ₂ -8:2 FTOH	¹³ C ₂ -8:2 FTOH	¹³ C ₂ -PFHxA	¹³ C ₄ -PFOA	¹³ C ₂ -PFDA
Range	66-138	61-119	69-124	73-122	68-125
Average \pm <i>S.D.</i>	96 \pm 28	98 \pm 17	90 \pm 18	96 \pm 16	104 \pm 17

3.3.7 Human Exposure Assessment

3.3.7.1 Inhalation Pathways

Concentrations of FTOHs and PFCAs in air samples in this study were used to estimate human exposure to these compounds *via* inhalation pathways. FTOHs and PFCAs concentrations below *MDLs* were assigned as half of *MDL* value for intake calculation. Two exposure scenarios (mean and worst scenarios) were assumed and the exposure was assessed for adult and toddlers (1-3 years). The inhalation intakes of FTOHs and PFCAs were calculated using equation 3.1 (eq. 3.1) (Shoeib *et al.*, 2011; Jogsten *et al.*, 2012; Kim *et al.*, 2012).

$$I_{air} = R_{outdoor} \left(\frac{C_{air} \times Q_{air} \times F_{uptake}}{BW} \right) + R_{indoor} \left(\frac{C_{air} \times Q_{air} \times F_{uptake}}{BW} \right) \quad \text{eq. 3.1}$$

Where I_{air} is inhalation intake (ng/kg-day), C_{air} is concentrations of FTOHs or PFCAs in outdoor and indoor air (ng/m³), Q_{air} is a volume inhaled rate (m³/day), F_{uptake} is an uptake fraction of the compounds (unitless), BW is body weight (kg), and R_{indoor} and $R_{outdoor}$ are time spend in indoor and outdoor, respectively. **Table 3.5** summarize parameters for calculation of inhalation intakes in each scenario.

Table 3.5 Values for estimation of daily intakes of FTOHs and PFCAs by inhalation pathways

Variables	Ranges	Mean scenario	Worst scenario	Brief rationale/ references
Daily inhalation volume (m ³ /day):				
- Adult	14.6-24	14.6	24	Allan and Richardson, 1998 ref. in Jogsten <i>et al.</i> , 2012
- Toddler	9.3-15	9.3	15	
Time spends in outdoor/ indoor (%)				
- Outdoor	10	10	10	Klepeis <i>et al.</i> , 2001 ref. in Jogsten <i>et al.</i> , 2012
- Indoor	90	90	90	
Uptake fraction (unitless):				
- FTOHs	0.38-1	0.38	1	Fasano <i>et al.</i> , 2006; Shoieb <i>et al.</i> , 2011; Jogsten <i>et al.</i> , 2012
- PFCAs	0.8-1	0.8	1	
Body weight (kg):				
- Adult	57.4-68.8	63	63	- NECTEC, 2009
- Toddler	-	12	12	- http://www.healthcarethai.com

3.3.6.2 Other Exposure Pathways

In this study, other exposure pathways to PFCAs in Thailand were assessed for consideration of overall exposure and for comparison purposes. Intakes of PFCAs from dust ingestion and drinking water consumption were calculated using eq. 3.2 and eq. 3.3, respectively.

$$I_{dust} = \frac{C_{dust} \times Q_{dust} \times F_{uptake}}{BW} \quad \text{eq. 3.2}$$

$$I_{water} = \frac{C_{water} \times Q_{water} \times F_{uptake}}{BW} \quad \text{eq. 3.3}$$

Where I_{dust} is an intake of PFCAs from dust ingestion (ng/kg-day), C_{dust} is concentrations of PFCAs in dust (ng/g), Q_{dust} is a dust ingested rate (g/day), F_{uptake} is an uptake fraction of PFCAs (unitless), BW is body weight (kg), I_{water} is an intake of PFCAs from drinking water (ng/kg-day), C_{water} is concentrations of PFCAs in drinking water (ng/L) and Q_{water} is a consumption rate of drinking water (L/day). **Table 3.6** summarize parameters for calculation of PFCAs intakes from dust ingestion and drinking water consumption in each scenario.

Table 3.6 Values for estimation of daily intakes of FTOHs and PFCAs by dust ingestion and drinking water consumption

Variables	Ranges	Mean scenario	Worst scenario	Brief rationale/ references
Concentration in dust (ng/g):				
- PFOA	<0.98-290	45	290	Goosey and Harrad, (2011)
Dust ingestion rate (mg/day):				
- Adult	4.16-110	50	110	Shoeib <i>et al.</i> , 2011
- Toddler	68-224	100	200	
Concentration in drinking water (ng/L):				
- ΣPFCA	-	11.5	11.5	Kunacheva, 2009
- PFOA	-	10.6	10.6	
Drinking water consumption (L/day):				
- Adult	1.3-1.41	1.3	1.41	US.EPA, 1997 ref. in Jogsten <i>et al.</i> , 2012; Egeghy and Lober, 2010 ref. in Haug <i>et al.</i> , 2011
- Toddler	-	0.4	0.4	

3.4 Results and Discussion

3.4.1 Concentrations of FTOHs and PFCAs in Outdoor and Indoor Air

FTOHs and PFCAs were detected from every outdoor and indoor air sampling site in Thailand, which indicated their contamination in the study areas (**Fig. 3.3**). Total concentration of three FTOHs in gas- and particle-phase (Σ FTOH) ranged from 1,690 to 13,030 pg/m^3 . All FTOHs were detected in 100% of the air samples. Total concentration of eight PFCAs in particle-phase (Σ PFCA) were 4-110 pg/m^3 , which were about two orders of magnitude lower than FTOHs concentrations. All PFCAs were detected >90% of the samples, except for PFDoDA, which were below its *MDL* (<0.39 pg/m^3). Concentrations of FTOHs and PFCAs at each sampling site are given in **Appendix E**.

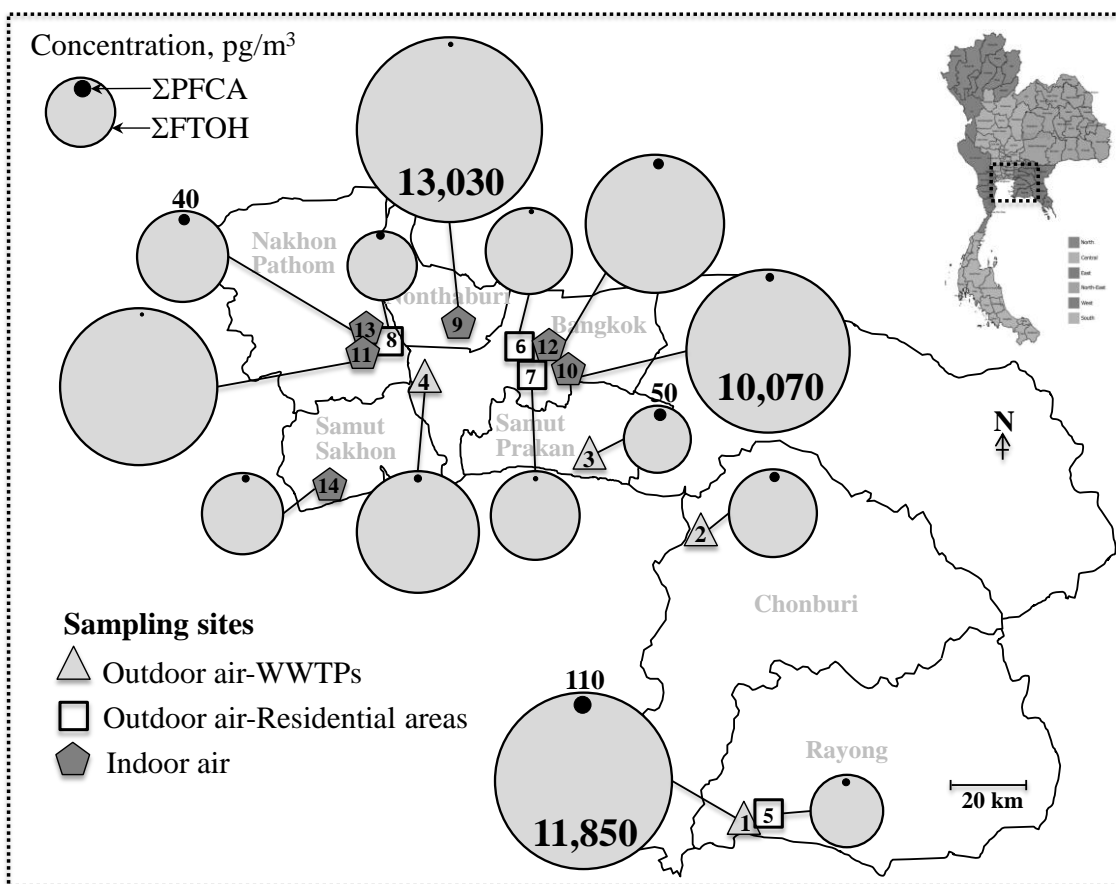


Figure 3.3 Distribution of FTOHs and PFCAs in the study area

Among outdoor air sampling sites, the highest concentration of FTOHs and PFCAs was detected at an aeration tank of industrial WWTP1. Wastewater might contain FTOHs and PFCAs, and they could be released to the air by aeration process, which was reported by a previous study (Vierke *et al.*, 2011). In the other hand, they might be emitted from chemical industries, the highest proportion of industrial type (Table 3.1), located in the industrial estate1 (IE1). For identifying point sources of these pollutants from industries to the environment, additional air and water monitoring at various industrial types/ activities are needed. At residential areas (RA), Σ FTOH in urban areas (RA2 = 2,830 pg/m³ and RA3 = 3,020 pg/m³) were higher than those in suburban area (RA4 = 1,830 pg/m³). High population density area could be a significant source of FTOHs emission to atmosphere, which was also reported by previous studies (Stock *et al.*, 2004; Jahnke *et al.*, 2007b).

For indoor air sampling sites, high concentrations of Σ FTOH (7,260-13,030 pg/m³) were detected in a condominium, a printing shop and offices, which were higher than outdoor residential areas (1,830-3,020 pg/m³), where these indoor sites were located. High FTOHs concentrations in indoor air, compared to outdoor air indicated possibility of indoor emission sources, which was also reported by previous studies (Shoeib *et al.*, 2011; Langer *et al.*, 2010; Barber *et al.*, 2007). FTOHs are used as surfactants in several products such as carpet, textile, paper, paints, coatings and adhesives, and there is potential for residual FTOHs (unreacted and unbound) to be released from these products (Dinglasan and Mabury, 2006).

Figure 3.4 shows composition profiles of FTOHs and PFCAs in the study areas. Dominant compounds in each sampling site were different. Among FTOHs, 10:2 FTOH (26-76%) was the dominant compound in most sites, followed by 8:2 FTOH (14-55%). For PFCAs, PFOA (9-72%) and PFHxA (3-50%) were dominant compounds. The results showed variable profiles among the sampling sites. This variation patterns might be caused by the variety of their emission sources in the measurement areas.

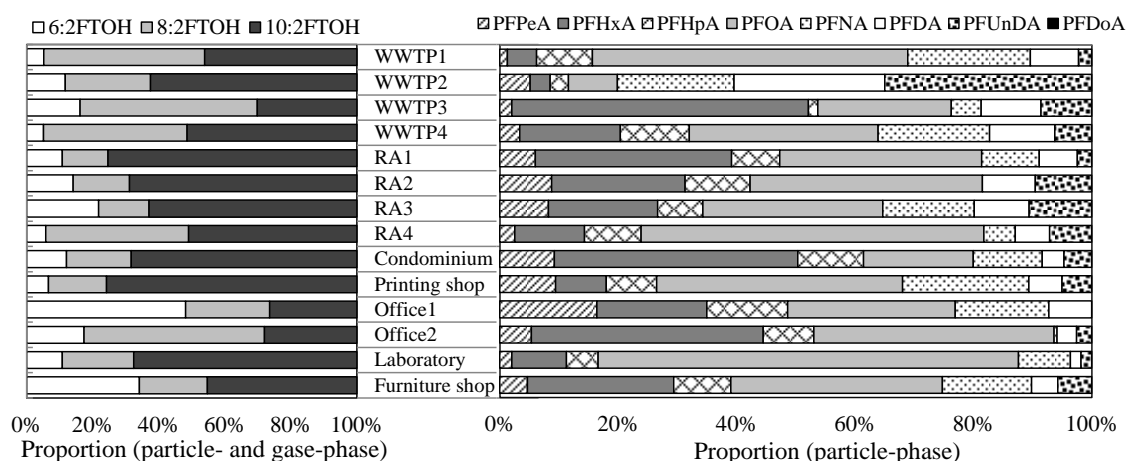


Figure 3.4 Composition profiles of FTOHs and PFCAs in study areas

3.4.2 Comparison of FTOHs and PFCAs in Thailand and other Countries

Comparison of Σ FTOH in outdoor air in Thailand and other countries is shown in **Fig. 3.5**. The concentrations at WWTPs in Thailand were two times lower than those in Canada (Vierke *et al.*, 2011). For residential areas sampling sites, Σ FTOH in Thailand were higher than those in most of the sampling sites in developed countries *i.e.* U.S. (Stock *et al.*, 2004), U.K. (Barber *et al.*, 2007), Canada (Shoeib *et al.*, 2011; Stock *et al.*, 2004), Germany (Jahnke *et al.*, 2007) and Japan (Oono *et al.*, 2008a; Oono *et al.*, 2008a), except in Korea, where high concentrations were detected at industrial areas (Kim *et al.*, 2012).

Figure 3.6 shows comparison of Σ FTOH in indoor air in Thailand and other countries. For some indoor air sampling sites (*i.e.* condominium and offices), Σ FTOH in Thailand were at the similar magnitude with developed countries *i.e.* Korea (Kim *et al.*, 2012), Japan (Liu *et al.*, 2013), Norway (Barber *et al.*, 2007; Huber *et al.*, 2011; Haug *et al.*, 2011), Canada (Shoeib *et al.*, 2011) and Germany (Langer *et al.*, 2010). However, for other indoor places (*i.e.* printing shop and furniture shop), the concentrations in Thailand were lower than those in Germany (Langer *et al.*, 2010). PFCAs concentrations in outdoor and indoor air in this study were about two orders of magnitude lower than FTOHs, which were also reported in most of the mentioned studies. Therefore, high concentration levels of airborne FTOHs might have high possibility for contribution to PFCAs contamination in environment.

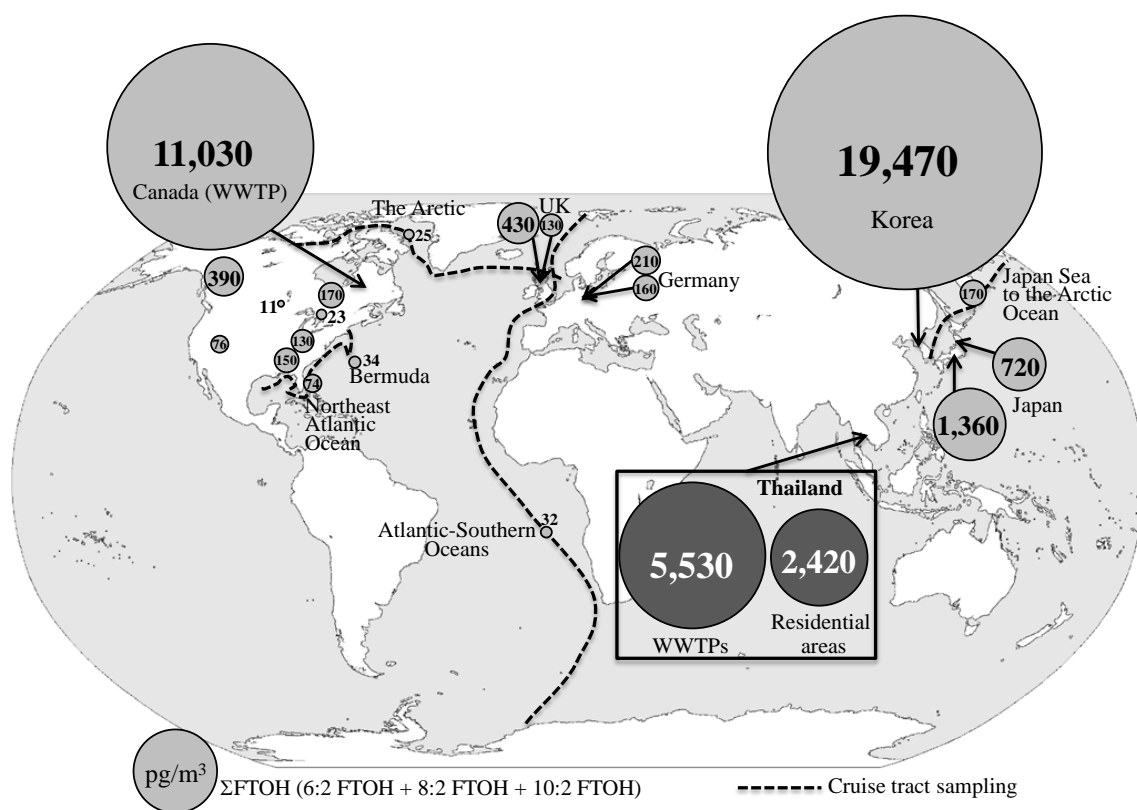


Figure 3.5 Comparison of Σ FTOH in outdoor air in Thailand and other countries

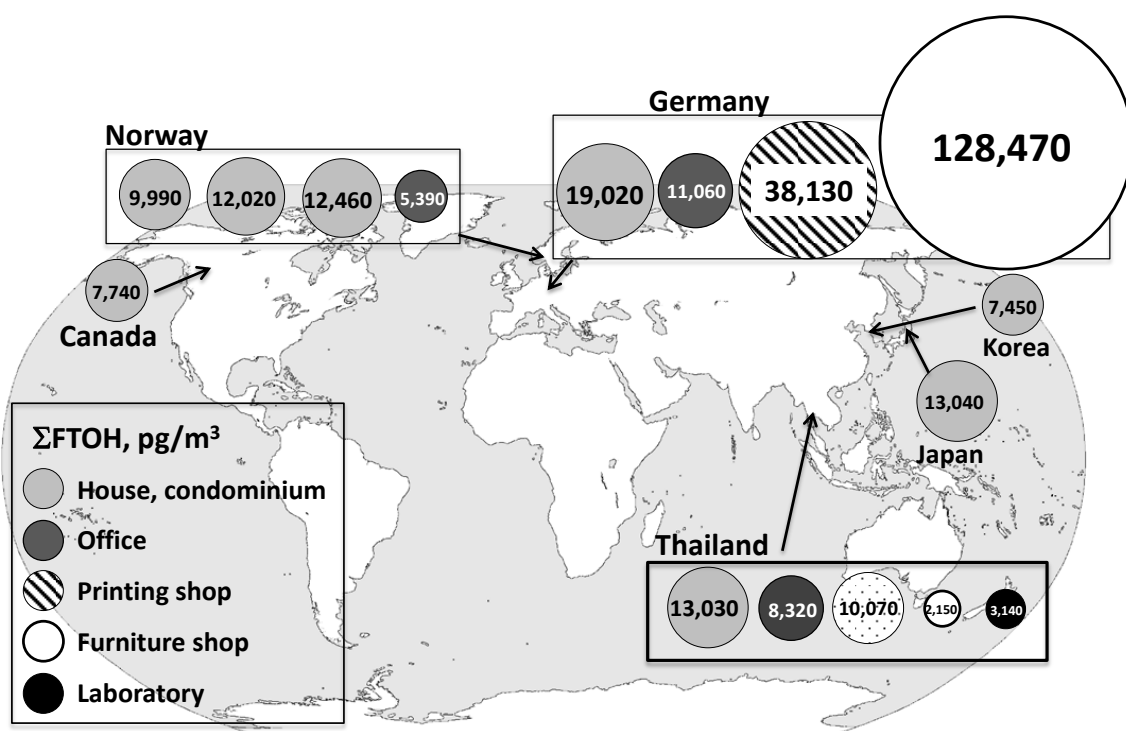


Figure 3.6 Comparison of Σ FTOH in indoor air in Thailand and other countries

3.4.3 Temporal Variation and Possible Sources

3.4.3.1 Temporal Variation of FTOHs and PFCAs in Air

Concentrations of FTOHs and PFCAs for seven consecutive days at three sampling sites *i.e.* the industrial wastewater treatment plant (WWTP1), the industrial area (RA1) and the roadside in urban area (RA2) are shown in **Fig 3.7** and detailed in **Appendix E**. Higher Σ FTOH (10,210-15,840 pg/m^3) and Σ PFCA (96-160 pg/m^3) were observed at WWTP1, compared to RA1 (Σ FTOH = 2,780-11,330 pg/m^3 , Σ PFCA = 2.4-4.7 pg/m^3) and RA2 (Σ FTOH = 1,560-7,210 pg/m^3 , Σ PFCA = 1.5-3.5 pg/m^3). Industrial wastewater is suggested as a point source of FTOHs emission to atmosphere *via* aeration process. An air sampler was set up at the aeration tank of WWTP1 and the results showed that this point source continue to emit FTOHs and PFCAs to atmosphere. Variation of FTOHs was observed at RA1 and RA2, which might be affected by their multiple sources and meteorological conditions. Details of factors influencing their occurrence in air were discussed in next sections.

3.4.3.2 Possible Sources of Airborne FTOHs and PFCAs

Relationship between each target compound was analyzed using Pearson correlation. FTOHs and PFCAs concentrations below *MDLs* were not assigned for statistical analysis. Correlation coefficient (*R*) among each target compound for each sampling site (WWTP1, RA1, RA2) are detailed in **Appendix F**. Strong correlation ($R > 0.7$) was found among long chain PFCAs (*i.e.* PFOA, PFNA, PFDA, PFUnDA and PFDoDA) at WWTP1, which indicated common sources of these PFCAs in the area. Scatter plots between these target compounds at WWTP1 and their correlation coefficient (*R*) are shown in **Fig. 3.8**.

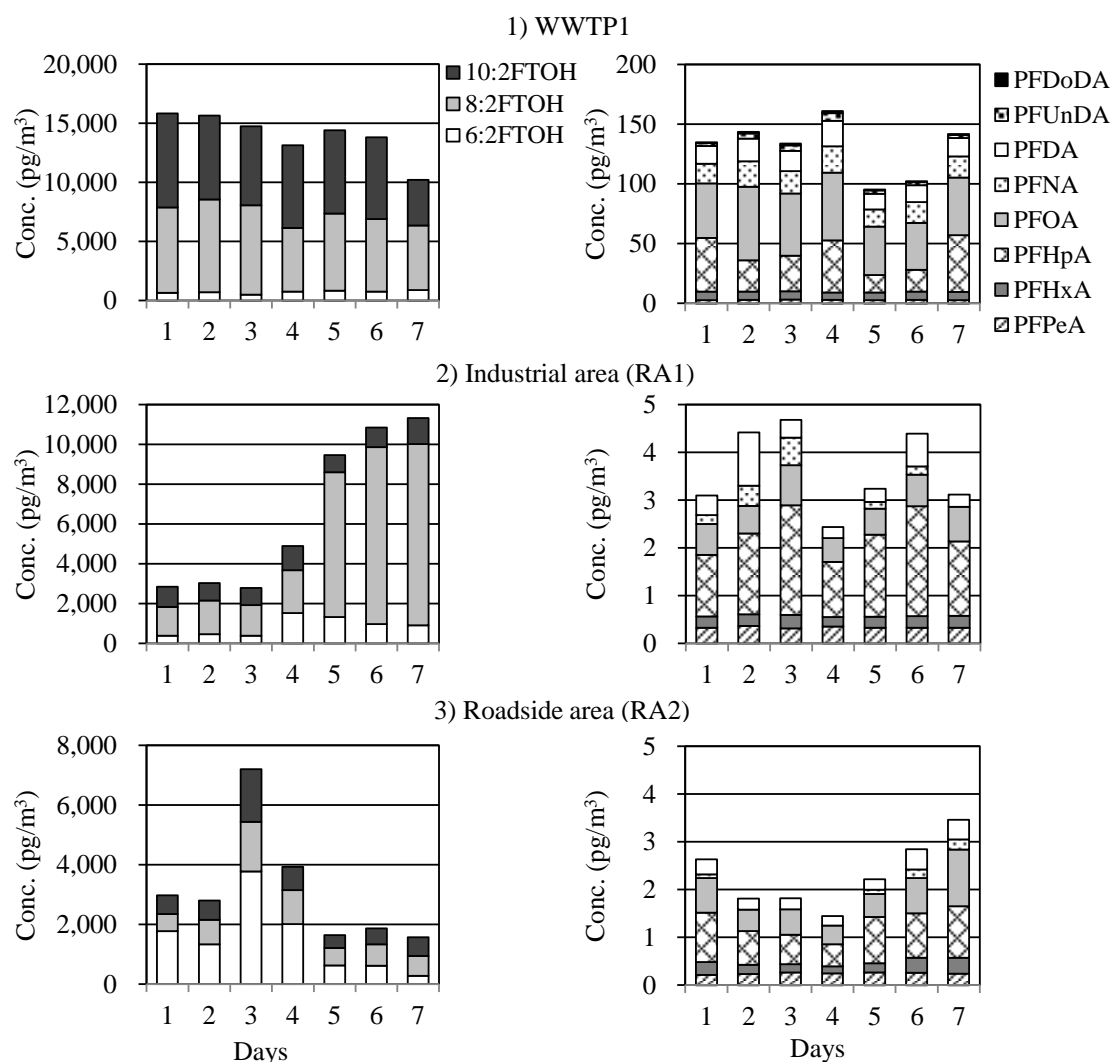


Figure 3.7 Temporal variations of FTOHs and PFCAs

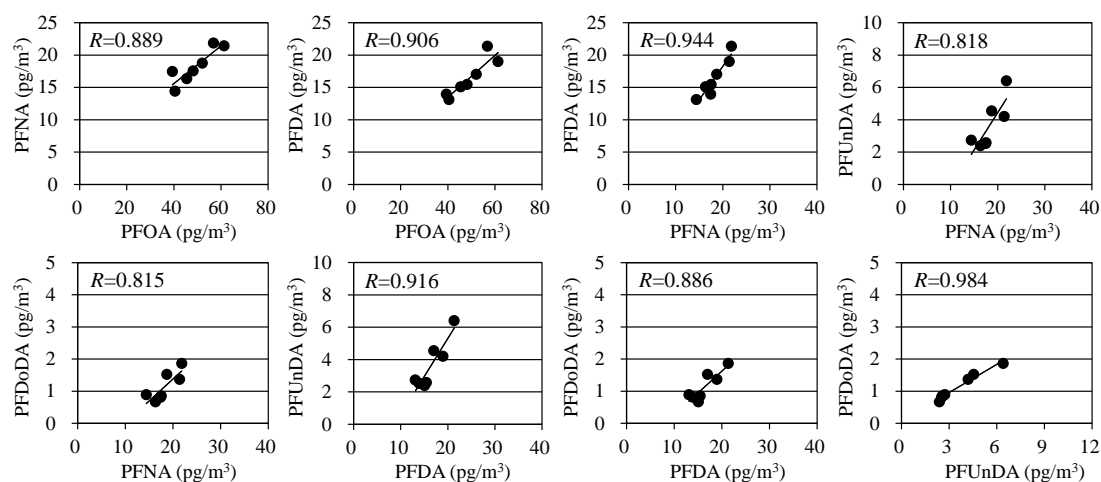


Figure 3.8 Scatter plots between target compounds at WWTP1

At RA1, strong correlation was found among PFHxA, PFHpA, PFOA and PFNA (**Fig. 3.9**), which indicated their common sources in the area. At RA2, strong correlation was found among two compound groups (**Fig. 3.10**). First group was among three FTOHs (6:2 FTOH, 8:2 FTOH and 10:2 FTOH) and second one was five PFCAs (PFHxA, PFHpA, PFOA, PFNA and PFDA). Strong correlation among these compounds indicated that they might be emitted from common sources.

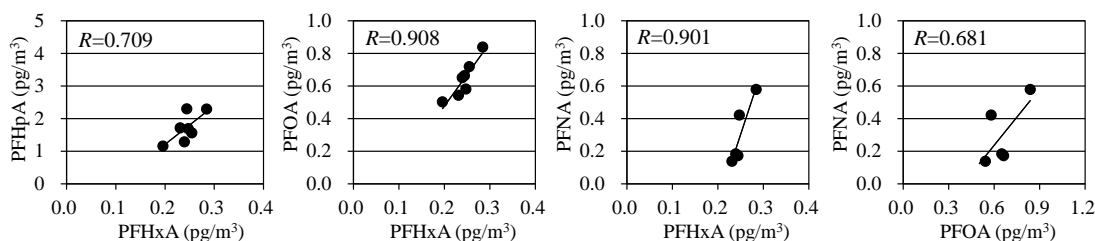


Figure 3.9 Scatter plots between target compounds at RA1

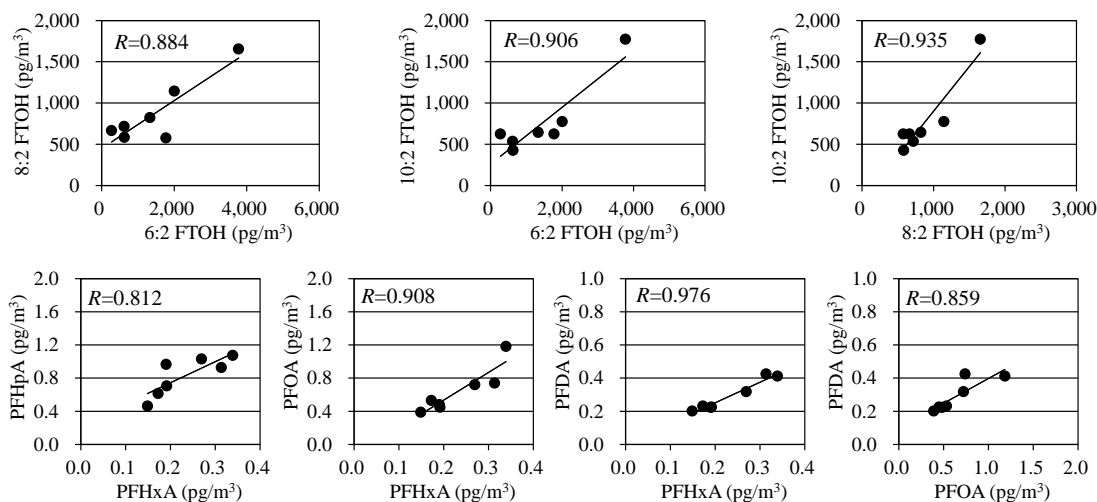


Figure 3.10 Scatter plots between target compounds at RA2

Most of correlation coefficient (R) between FTOHs and PFCAs was very low for all three sampling sites which indicated different emission sources among FTOHs and PFCAs, except for 8:2 FTOH and PFNA at RA2 ($R=0.850$). RA2 was a roadside site in an urban area which motor vehicles were the main emission sources in the area. PFCAs and FTOHs are used in manufacturing process of motor vehicles such as paint sealant coating, oil additives and brake parts (Harada *et al.*, 2005).

For identification of possible sources of FTOHs, five commercial products *i.e.* car wax, leather and vinyl polish, and glass shield were collected from Thailand as detailed in **Table 3.7**. They were prepared and analyzed for FTOHs by extraction (wax products) or dilution (liquid products) method using methanol. Analysis of FTOHs was conducted by GC-MS. FTOHs were detected in only car wax (2), which the content of 6:2 FTOH, 8:2 FTOH and 10:2 FTOH was 0.58 $\mu\text{g/g}$, 0.89 $\mu\text{g/g}$ and 0.84 $\mu\text{g/g}$ of the product, respectively. This screening result confirms possible sources of FTOHs from commercial products.

Table 3.7 Possible sources of FTOHs from commercial products in Thailand

Products	Production data	Phase of product
Car wax (1)	imported from U.S.A	wax
Car wax (2)	No data	wax
Leather & vinyl polish (1)	produced in Thailand	liquid
Leather & vinyl polish (2)	imported from France	liquid
Glass shield	No data	liquid

3.4.4 Behaviors and Factors Influencing Occurrences in Air

3.4.4.1 Gas- and Particle-Phase Partitioning

For phase partitioning, FTOHs were dominant in gas-phase fractions as shown in **Fig.3.11**. Gas-phase fraction of 6:2 FTOH, 8:2 FTOH and 10:2 FTOH ranged 96-100%, 90-100% and 85-100% of total concentrations, respectively. This study found that particle-phase FTOHs increased with increasing of fluorocarbon chain. As a result, detection of 6:2 FTOH, 8:2 FTOH and 10:2 FTOH in particle-phase was 14%, 43% and 46% of the samples, respectively.

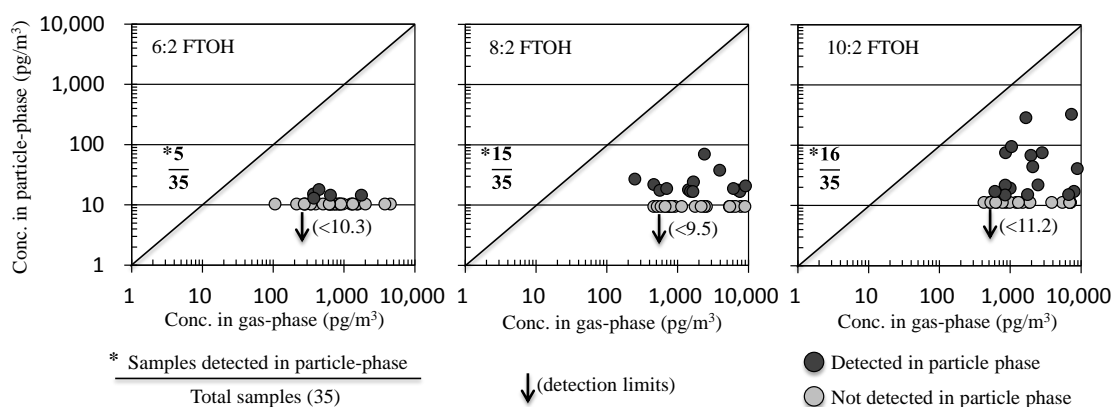


Figure 3.11 Gas- and particle-phase of FTOHs in air samples in the study areas

3.4.4.2 Correlation between FTOHs/PFCAs and Total Particulate Matter

Relationship between target compounds and total particulate matter (TPM) were analyzed using Pearson correlation. TPM was determined by weighting GFFs before and after air sampling in this study. FTOHs and PFCAs concentrations below *MDLs* were not assigned for statistical analysis. **Figure 3.12** show scatter plots between particle-phase FTOHs and TPM and **Fig. 3.13** show the plots between particle-phase PFCAs and TPM. No correlation was found between particle-phase FTOHs/ PFCAs and TPM. These results indicated that particle mass might not be a governing factor on particle-phase fractions of FTOHs and PFCAs. The fractions might be influenced by other factors such as chemical compositions and sources of particles.

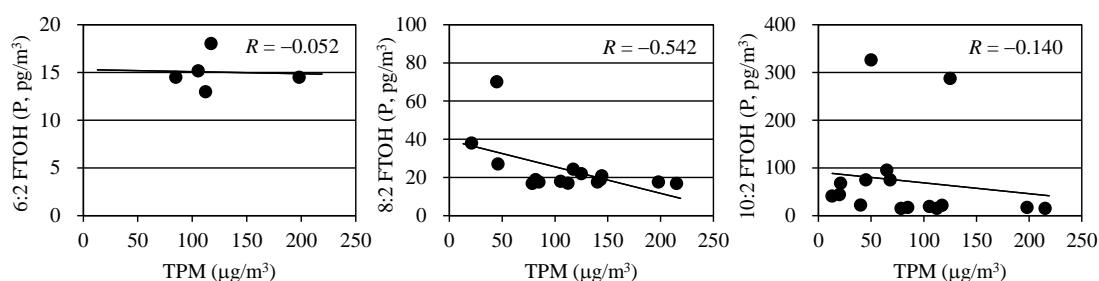


Figure 3.12 Scatter plot between particle-phase FTOHs and TPM

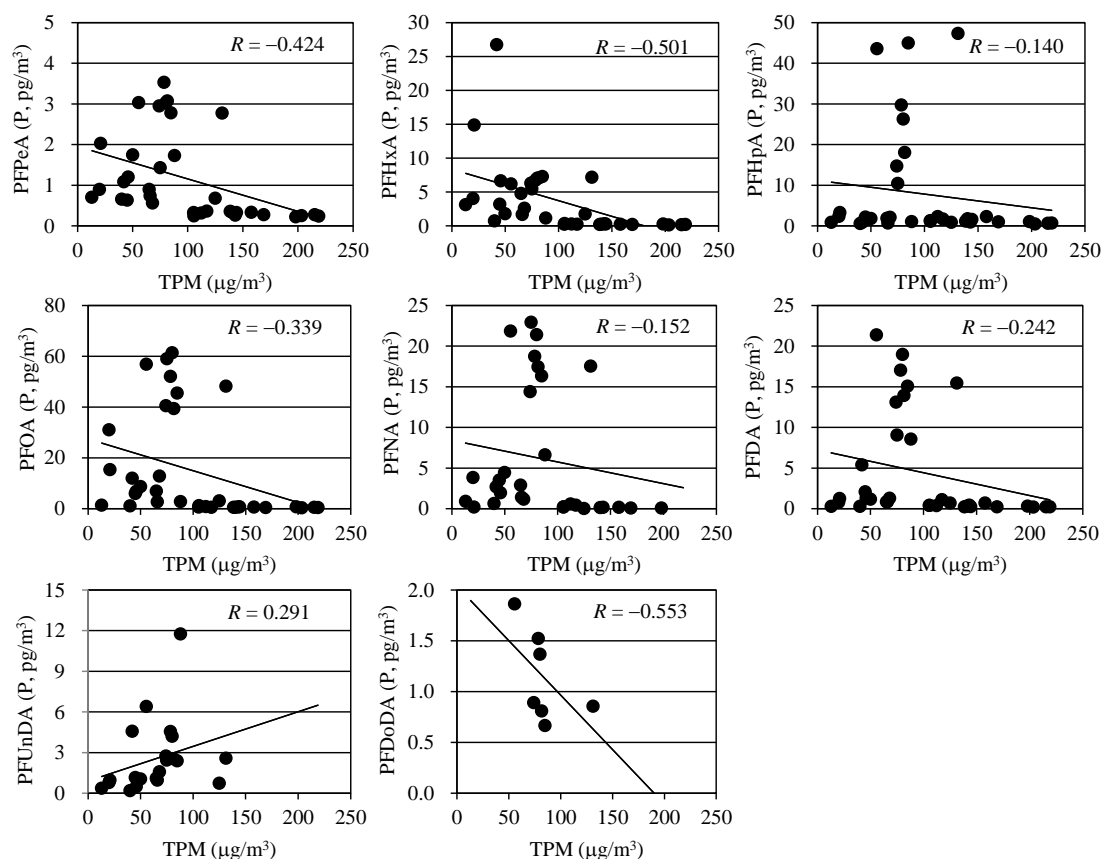


Figure 3.13 Scatter plot between particle-phase PFCAs and TPM

3.4.4.3 Correlation between FTOHs/PFCAs and other Air Pollutants

Correlation between target compounds and other air pollutants were analyzed using Pearson correlation. Other pollutants *i.e.* carbon monoxide (CO), nitrogen dioxide (NO₂), sulfur dioxide (SO₂), total hydrocarbons (THC), methane (CH₄), ozone (O₃) and 18 VOCs were observed by Pollution Control Department (PCD), Thailand. Most of them were available for all three sampling sites (WWTP1, RA1 and RA2), except for VOCs which were available only WWTP1 and RA1. Details of their concentrations are given in **Appendix G**. FTOHs and PFCAs concentrations below *MDLs* were not assigned for statistical analysis. Correlation coefficient (*R*) between target compounds and other pollutants are given in Appendix F. Most of the results showed that no strong correlation ($R > 0.7$) was found between them. Moderate correlation ($0.4 < R < 0.7$) was found between 6:2 FTOH and some VOCs (**Fig. 3.14**). These results indicated possibility of their common emission sources, which were suspected to be from industrial sectors.

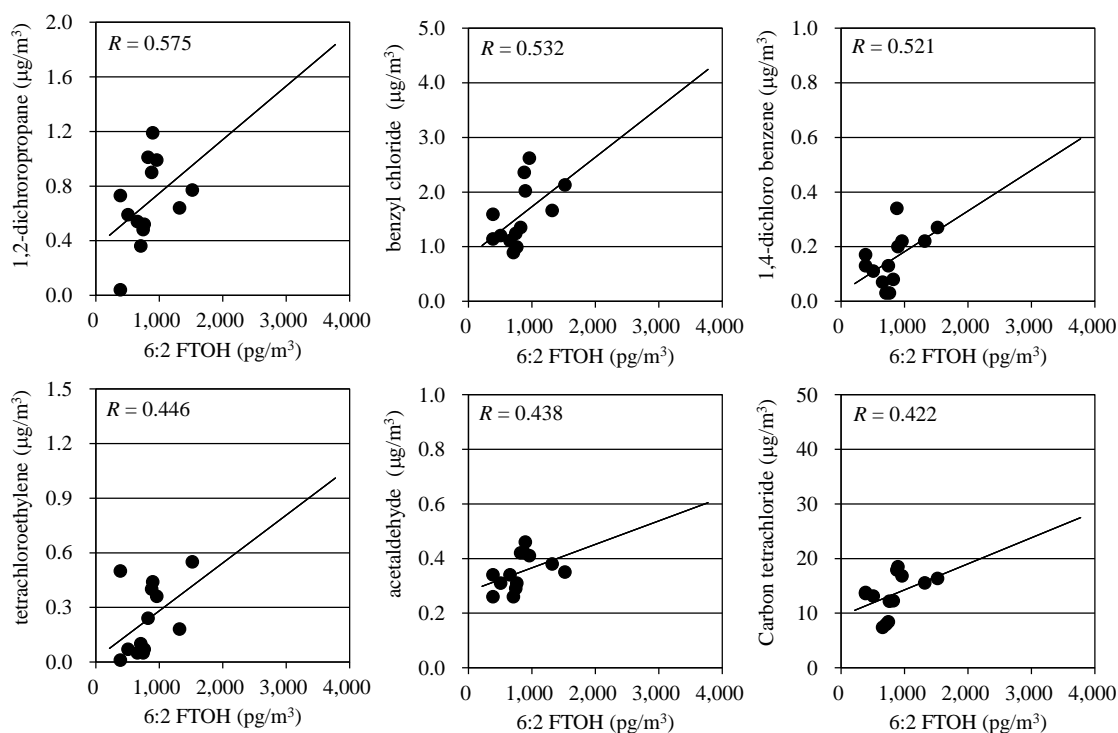


Figure 3.14 Scatter plot between 6:2 FTOH and volatile organic compounds

3.4.4.4 Correlation between FTOHs/PFCAs and Meteorological Parameters

Relationship between target compounds and meteorological parameters *i.e.* wind speed, temperature, relative humidity, solar radiation and rain amount were analyzed using Pearson correlation. Details of meteorological parameters are given in Appendix G. Correlation coefficient (R) between them is shown in Appendix F. Moderate correlations ($0.4 < R < 0.7$) were shown between most of target compounds and wind speed and relative humidity (**Fig 3.15**). Presence of target compounds in the air environment might be affected by these parameters.

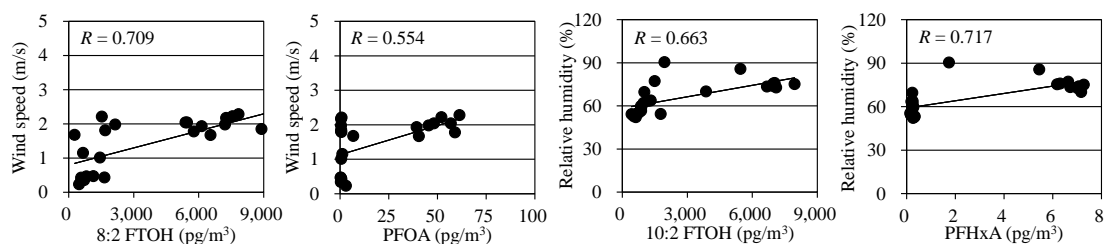


Figure 3.15 Scatter plot between target compounds and meteorological parameters

3.4.5 Daily Intakes of FTOHs and PFCAs

Results of daily intakes of FTOHs and PFCAs in Thailand were shown in **Table 3.8**. Inhalation intakes of FTOHs were about two orders of magnitude higher than those of PFCAs for both adults and toddler. In mean scenario, inhalation intakes of FTOHs for adult was 0.636 ng/kg-day (or 40 ng/day), whereas the intakes of PFCAs was 0.004 ng/kg-day (or 0.25 ng/day). Inhalation intake of FTOHs in this study was consistent with the previous study (43 ng/day) in Vancouver, Canada (Shoeib *et al.*, 2011) which also had reported high exposure risk for adults and toddler by inhalation intake of precursor compounds. A high intake of FTOHs, 4.2 ng/kg-day or 264 ng/day was also reported in Korea (Kim *et al.*, 2012). Total intake of PFCAs and FTOHs by four exposure pathways for Thai people was 4.909 ng/kg-day.

Table 3.8 Daily intakes of FTOHs/ PFCAs for different exposure pathways in Thailand

Pathways	Compounds	Daily Intakes (ng/kg-day)			
		Mean scenario		Worst scenario	
		Adult	Toddler	Adult	Toddler
Air inhalation	FTOHs	0.636	2.125	4.923	16.153
	PFCAs	0.004	0.015	0.019	0.063
	PFOA	0.002	0.007	0.013	0.042
Dust ingestion	PFOA	0.029	0.150	0.506	4.833
Drinking water consumption	PFCAs	0.190	0.307	0.257	0.383
	PFOA	0.175	0.283	0.237	0.353
Food consumption ^{1/}	PFCAs	4.050	-	-	-
	PFOA	0.150	-	-	-

Note: ^{1/} Thirteen food groups were collected from Nakhonpathom province, Central of Thailand during 2012. Foods included rice, potato, cooking oil, peanuts, guava carrot, kale, beer, shrimp, beef, skim milk, red chili and cookies (Ando *et al.*, 2012).

There were studies about contamination of PFCAs in Thailand's environment such as house dust (Goosey and Harrad, 2011), drinking water (Kunacheva *et al.*, 2010) and food (Ando *et al.*, 2012) but measurements of FTOHs in these environmental media have not been reported yet. For comparison purpose, intakes of PFCAs by dust ingestion and drinking water consumption were calculated using the concentrations from the previous mentioned studies (Table 3.8). Intake of PFOA (mean scenario for

adults) was 0.029 ng/kg-day for dust ingestion and 0.175 ng/kg-day for drinking water consumption. Intake of PFOA by food consumption in Thailand was reported by Ando *et al.*, (2012), which was 0.150 ng/kg-day. As the results, contribution of PFOA intakes by air inhalation (1%) and dust consumption (8%) were insignificant compared to drinking water (49%) and food consumption (42%). However, FTOHs biotransformation to PFCAs in animal tissues had been reported by previous studies (Martin *et al.*, 2005; Butt *et al.*, 2010). Thus, air inhalation of FTOHs might be a significant pathway to contribute to PFCAs exposure for Thai people.

3.5 Summary

FTOHs and PFCAs were detected at every outdoor and indoor air sampling site, which illustrated their contamination in the study areas. Concentrations of FTOHs (1,690-13,030 pg/m³) were about two orders of magnitude higher than the concentrations of PFCAs (4-110 pg/m³). Therefore, high concentration levels of airborne FTOHs might have high potential contribution to PFCAs contamination in environment. This study conducted first investigation of FTOHs and PFCAs in air in Asian developing countries. Compared the concentrations to developed countries, outdoor FTOHs in Thailand were found in higher level in most of other countries, while indoor FTOHs were found at the similar high levels as the developed countries.

Composition profiles of FTOHs and PFCAs varied among outdoor and indoor air in Thailand. 10:2 FTOH (26-76%) and 8:2 FTOH (14-55%) were dominant compounds among FTOHs in most sampling sites, whereas PFOA (9-72%) and PFHxA (3-50%) were the dominant compounds among PFCAs. The substances' different distribution patterns might be caused by the variety of their emission sources in the measurement areas.

The highest outdoor concentration of FTOHs (11,850 pg/m³) and PFCAs (110 pg/m³) was detected at an industrial WWTP1. This suggested possible sources of FTOHs and PFCAs from an industrial sector. Seven consecutive days monitoring of FTOHs (10,210-15,840 pg/m³) and PFCAs (96-160 pg/m³) at an aeration tank of WWTP1 indicated their continuous emission to atmosphere. Therefore, wastewater treatment

plants induced by aeration process are an important source of FTOHs and PFCAs from industrial sectors. High correlation ($R > 0.7$) among long chain PFCAs (C8-C12) at WWTP1 indicated their common sources in the area.

Higher concentrations of FTOHs were detected in urban sites ($RA2=2,830 \text{ pg/m}^3$, $RA3=3,020 \text{ pg/m}^3$) than in a suburban site ($RA4=1,830 \text{ pg/m}^3$), which demonstrated influence of possible sources from high populated areas. Detection of 6:2 FTOH ($0.58 \text{ }\mu\text{g/g}$), 8:2 FTOH ($0.89 \text{ }\mu\text{g/g}$) and 10:2 FTOH ($0.84 \text{ }\mu\text{g/g}$) in a product of car wax, which collected from convenience stores in Thailand, confirmed their sources by motor vehicles. High correlation ($R > 0.8$) among FTOHs compounds was observed at roadside in urban area ($RA2$) indicated their common sources in the area.

Particle-phase FTOHs increased with increasing fluorocarbon chain by which 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were partially detected in 14%, 43% and 46% of the samples, respectively. No correlations were found between particle-phase target compounds and total particulate matter. These results indicated that particle mass might not be a governing factor on particle-phase fractions of FTOHs and PFCAs. The fractions might be influenced by other factors such as chemical compositions and sources of particles. There were no clearly correlation between target compounds and meteorological parameters (*i.e.* temperature, solar radiation and rainfall). However, moderate correlation was shown between some target compounds and wind speed/relative humidity.

For exposure assessment in mean scenario for adult, intake of FTOHs and PFCAs was 0.636 ng/kg-day and 0.004 ng/kg-day , respectively. For comparison purpose, contribution of PFOA intakes by air inhalation (0.002 ng/kg-day , 1%) and dust ingestion (0.029 ng/kg-day , 8%) were insignificant compared to drinking water (0.175 ng/kg-day , 49%) and food consumption (0.150 ng/kg-day , 42%). However, PFCAs exposure by inhalation of their precursor compounds should not be neglected because inhalation intake of FTOHs was much higher than those of PFCAs. Total intake of PFCAs and FTOHs by four exposure pathways for Thai people was 4.909 ng/kg-day , which not exceeded the most strict recommendation level (300 ng/kg-day).

Chapter 4

Industrial Sources of Airborne FTOHs and PFCAs in Japan

4.1 Introduction

For effective pollution controls, source reduction strategies are very crucial. PFCs have been widely used in several industrial and commercial products for over 50 years. Their contaminations were observed not only in aquatic environment but also in the atmosphere (Ahrens, 2011). Recently, FTOHs and PFCAs were detected in the air in several parts of the world but their emission sources remain unknown.

High concentrations of FTOHs and PFCAs in ambient air were detected at industrial areas (Kim *et al.*, 2012), roadside areas (Harada *et al.*, 2005) including in indoor air sampling sites (Barber *et al.*, 2007; Langer *et al.*, 2010; Shoeib *et al.*, 2011), which suggested their sources from these areas. Among Asian countries, Japan has strict environmental regulations and was a former country to recognize PFCs contamination in the environment. FTOHs and PFCAs were detected in outdoor air by national-wide survey of Japan (Harada *et al.*, 2006; Harada *et al.*, 2007; Oono *et al.*, 2008a; Oono *et al.*, 2008b). High concentrations of FTOHs were observed at Keihan area which is one of the major industrial zones in Japan, suggested a point source from this area. FTOHs were detected in 49 Japanese houses in Keihan area (Lie *et al.*, 2013) and the concentrations were significant higher than those in outdoor air, which suggested possible indoor emission sources in the area. However, industrial source emission to the air in Japan has not been well understood yet.

To identify emission sources of FTOHs and PFCAs from industrial sectors to atmosphere, air sampling was conducted in industries producing and using fluorotelomer compounds in Japan. Understanding these emission sources could provide further effective control measures in the industries.

4.2 Objectives

Objectives of this chapter were (1) to investigate airborne FTOHs and PFCAs levels in industries related fluorotelomer compounds, (2) to compare the concentration levels with a near-source site, a remote site and past studies, (3) to examine composition profiles and phase partitioning, and (4) to calculate inhalation intakes of FTOHs and PFCAs and their removal efficiency by air cleaner

4.3 Methodology

4.3.1 Air Sampling Locations

Four air sampling sites in Japan were selected as possible industrial sources of fluorotelomer compounds (Site A and Site B), a near-source site (Site C) and a remote site (Site D). Site A is a fluorotelomer compounds production industry and Site B is an industry which using fluorotelomer compounds in their production process. Site C is a residential area located near the industries and Site D located far from the industries which is representative for a clean area. Locations of air sampling sites in Japan are shown in **Fig. 4.1**.

At Site A, air samples were collected at 2 points which were (1) an inlet of wastewater treatment plant (WWTP) and (2) a sludge thickener unit. Three sampling points were selected for Site B; (1) WWTP, (2) an industrial process room and (3) rooftop of a building. These multiple point of sampling were conducted in order to specify emission point sources of FTOHs and PFCAs from the industries to the atmosphere. For Site C and Site D, the sampling points were set at the balcony and roof top of a building, respectively, in order to check the concentration in outdoor air of the areas. The sampling points at each site are concluded in **Table 4.1**.

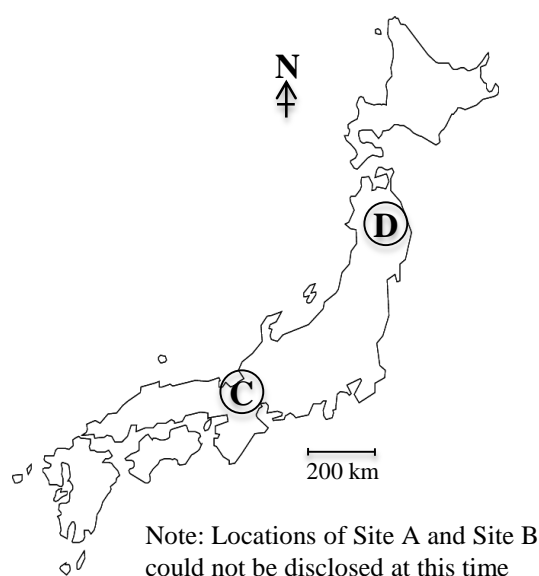


Figure 4.1 Air sampling locations in Japan

Table 4.1 Detail of air sampling locations and sampling time in Japan

Sites	Sampling Points	Sample Name	Sampling Date	Sampling Time	Air Volume (m ³)
A	(1) inlet of wastewater treatment plant	A(1)-1	October, 8 2013	1 hour	30
A	(1) inlet of wastewater treatment plant	A(1)-2	October, 8 2013	1 hour	30
A	(2) sludge thickener unit	A(2)-1	October, 8 2013	1 hour	30
A	(2) sludge thickener unit	A(2)-2	October, 8 2013	1 hour	30
A	(2) sludge thickener unit	A(2)-3	October, 8 2013	1 hour	30
B	(1) wastewater treatment plant	B(1)-1	July 9-10, 2012	24 hours	720
B	(1) wastewater treatment plant	B(1)-2	July 10-11, 2012	24 hours	720
B	(2) an industrial process room	B(2)	July 11-12, 2012	24 hours	720
B	(3) roof top of a building	B(3)-1	July 12-13, 2012	24 hours	720
B	(3) roof top of a building	B(3)-2	July, 13-14 2012	24 hours	720
C	2 nd floor's balcony of a building	C-1	June 15, 2013	12 hours	360
C	2 nd floor's balcony of a building	C-2	June 15-16, 2013	12 hours	360
D	roof top of a building	D-1	September 9-10, 2013	24 hours	720
D	roof top of a building	D-2	September 10-11, 2013	24 hours	720
D	roof top of a building	D-3	September 11-12, 2013	24 hours	720

4.3.2 Setup of Air Cleaning

Field experimental removal of airborne FTOHs and PFCAs was conducted at the fluorotelomer compound production industry (site A) where had the highest concentrations of FTOHs and PFCAs. Air sampling and air cleaning were

simultaneously conducted in the sludge thickener room. Firstly, two air samples were collected to evaluate the concentrations of FTOHs and PFCAs in the room before air cleaning. Later, the air cleaner was turned on and four air samples were collected to evaluate performance of air cleaning. Setup of air sampler and air cleaner in the industry is shown in **Fig. 4.2**. Setup time for air sampling and air cleaning are shown in **Table 4.2**.

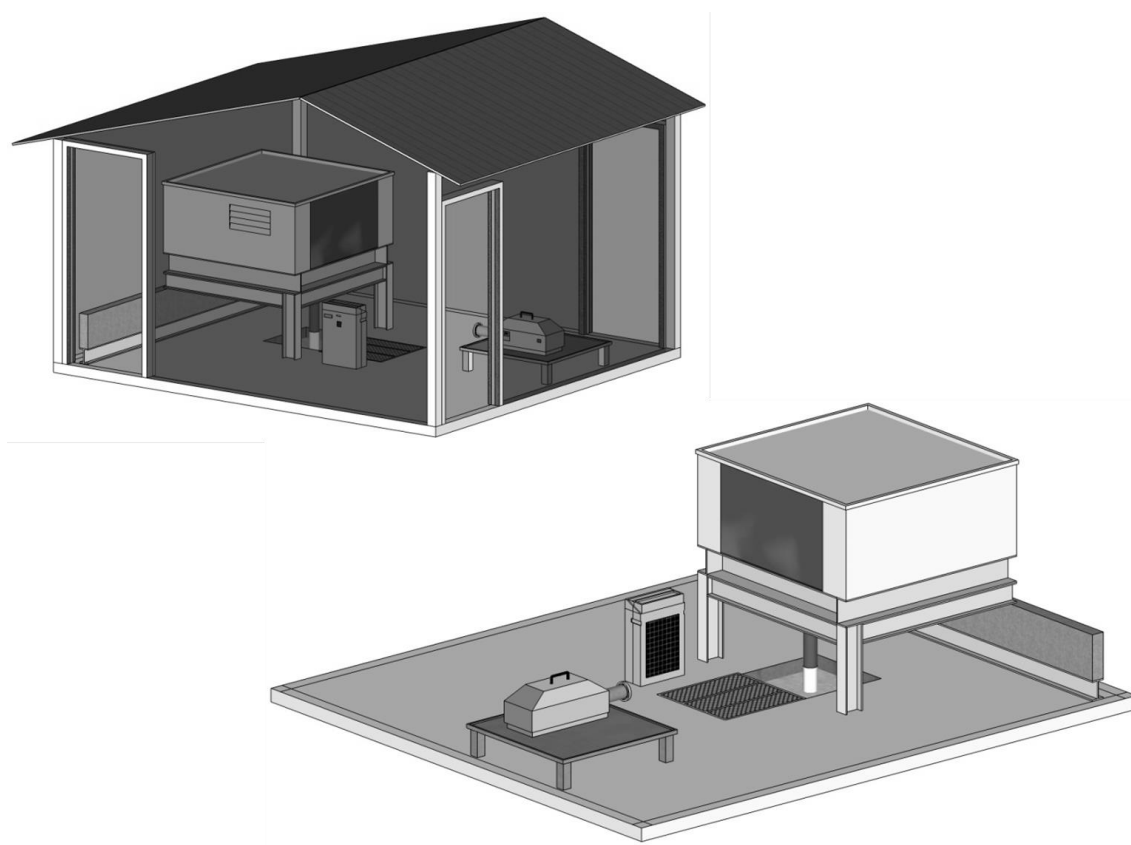


Figure 4.2 Setup of air sampler and air cleaner in an industry

Table 4.2 Setup time for air sampling and air cleaning

Time (February 20, 2014)	Air sampling	Air cleaning
10:40-11:40	Air sample 1 (AS1)	-
11:45-12:45	AS2	-
13:20-14:20	AS3	Turn on at 13:20
14:25-15:25	AS4	Operating
15:30-16:30	AS5	Operating
16:40-17:40	AS6	Turn off at 17:40

Air cleaner (Sharp FU-Z51CX) equip with activated carbon fiber (ACF) filter (vapor adsorption) and HEPA filter (glass fiber, 99.7% removal of 0.3 μm particles) was applied for removal of FTOHs and PFCAs from the air. Flow rate of air cleaning was set at 5.1 m^3/min . Air was passed through ACF and HEPA filter, respectively.

4.3.3 Air Sample Collection

Air samples were collected using a high volume air sampler (HV-500F, Sibata, Saitama, Japan) at flow rate of 500 L/min. Sampling times ranged 1-24 hours which were 30-720 m^3 of air volume (Table 4.1). This study adapted three types of media for air sampling; glass fiber filters (GFFs, GB100R grade, ϕ 110 mm, 0.6 μm pore size, Advantec®, Toyo Roshi Kaisha, Ltd., Tokyo, Japan), polyurethane foams (PUFs, ϕ 90 x 50 mm, Sibata, Saitama, Japan) and XAD-2 resin (Amberlite® XAD®-2, matrix styrene/divinylbenzene, Sigma-Aldrich, Tokyo, Japan). GFFs and PUFs were pre-cleaned by soaking them twice in ethyl acetate and 3 times in methanol. Soaking time was 1 hour for every process. PUFs were dried overnight at 60 °C in a drier while GFFs were heated at 250°C for 2 hours in an oven. XAD-2 resin was pre-cleaned in a Soxhlet extraction apparatus (**Appendix H**) by ethyl acetate (8 hour), followed by methanol twice (2x8 hour). Pre-cleaned media were wrapped in aluminum foil and sealed in zip lock polypropylene (PP) plastic bags for transportation to the sampling sites.

One set of the sampling media (GFF and PUF/XAD-2/PUF) was used to collect the target compounds at each sampling site. Particle-phase fractions of the target compounds were collected on a GFF, while the gas-phase fractions were trapped in a column of PUF/XAD-2/PUF. After sampling, these sampling media (air samples) were wrapped in aluminum foil, sealed in zip lock PP plastic bags and stored at 4°C until analysis. Another set of the sampling media was also prepared as a field blank to examine contamination during all of the procedures. The field blank set was handled with a completely same procedure as that for the sample set except that it was just placed close to the sampling points without installation in the vacuum pump for sampling.

4.3.4 Chemical and Standards

Eleven target compounds of three FTOHs (6:2 FTOH, 8:2 FTOH, 10:2 FTOH), eight PFCAs (PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDODA), and 8:1 FA (internal standard) were purchased from Wako Pure Chemicals (Osaka, Japan). Four mass-labeled ($^{13}\text{C}_2$ 8:2 FTOH, $^{13}\text{C}_2$ -PFHxA, $^{13}\text{C}_4$ -PFOA and $^{13}\text{C}_2$ -PFDA) were purchased from the Wellington Laboratory Inc. (Ontario, Canada). Analytical or HPLC grade were used for all solvents and reagents.

4.3.5 Sample Preparation

4.3.5.1 Air Sample Preparation

Each air sample was prepared for analysis of four portions; particle-phase FTOHs, gas-phase FTOHs, particle-phase PFCAs, and gas-phase PFCAs. Analytical procedures for FTOHs and PFCAs in air samples are shown in **Fig. 4.3**. For exaction of particle-phase FTOHs, a half of GFF was soaked in 10 mL methanol and shaken at 150 rpm for 1 hour. The extraction process was repeated 4 times (about 40 mL of extracts in total). For gas-phase FTOHs extraction, PUFs were soaked in 250 mL methanol and shaken at 150 rpm for 1 hour. Then, they were soaked in 150 mL methanol 3 more times (about 700 mL of extracts in total). XAD-2 was soaked in 50 mL methanol 4 times using Soxhlet apparatus (Appendix H) for 1 hour, and about 200 mL of extracts was obtained in total. Finally, both extracts were combined to make 900 mL of a gas-phase extract. Mass-labeled FTOH ($^{13}\text{C}_2$ 8:2 FTOH) was spiked into the sampling media before extraction to confirm the recovery. Extracts of particle and gas-phase FTOHs were separately evaporated to 3-5 mL using a rotary evaporator. After that, the concentrated solutes were cleaned up using 0.2 μm syringe filters and chemically dried using sodium sulfate (Na_2SO_4). The purified liquid extracts were concentrated to 1 mL under a gentle stream of nitrogen.

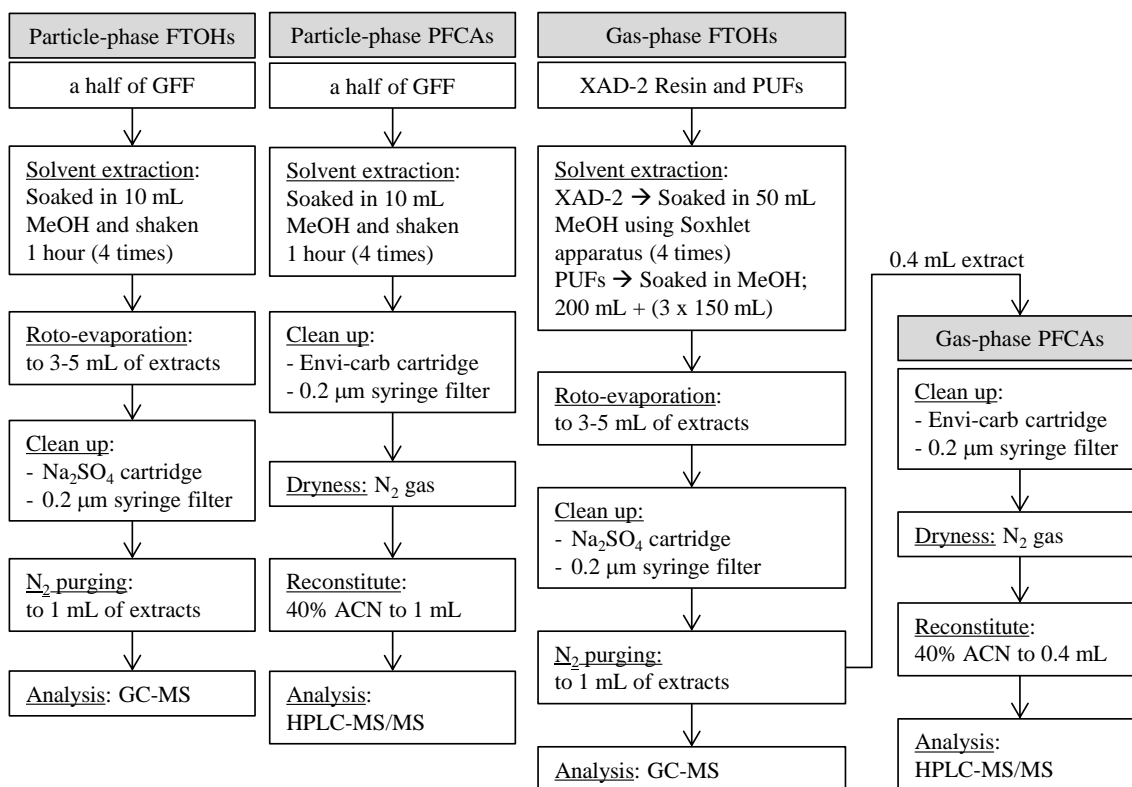


Figure 4.3 Analytical procedures for particle and gas-phase of FTOHs and PFCAs

The other half of GFF was used to determine particle-phase PFCAs. It was soaked in 10 mL methanol and shaken at 150 rpm for 1 hour. The extraction process was conducted 4 times (about 40 mL of extracts in total), and the extracts were passed through ENVI-carb cartridges (Sigma-Aldrich, Tokyo, Japan) to eliminate matrix. Then, the purified extracts were evaporated using nitrogen gas, and reconstituted to 1 mL of mobile phase of HPLC-MS/MS (40% acetonitrile in *ultrapure* water). Mass-labeled PFCAs ($^{13}\text{C}_2$ -PFHxA, $^{13}\text{C}_4$ -PFOA and $^{13}\text{C}_2$ -PFDA) were spiked into the sampling media before the extraction step to confirm their recoveries.

For extraction of gas-phase PFCAs, 0.4 mL of the purified liquid extracts of gas-phase FTOHs were passed through ENVI-carb cartridges to eliminate matrix. Then, the purified extracts were evaporated using nitrogen gas, and reconstituted into HPLC-MS/MS mobile phase to 0.4 mL.

4.3.5.2 Air Cleaner Sample Preparation

Activated carbon fiber (ACF) filter of air cleaner (AC) was pre-cleaned by soaking it in methanol and dried before using. After air cleaning, the ACF was soaked in 1,000 mL methanol for 1 hour, and the extraction was done for 4 times. The extracts were separately evaporated to 3-5 mL using a rotary evaporator. After that, the concentrated solutes were cleaned using 0.2 μm syringe filters and Na_2SO_4 to remove particles and water, respectively. The purified liquid extracts were concentrated to 1 mL under a gentle stream of nitrogen. For PFCAs extraction, 0.4 mL of the purified liquid extracts of FTOHs were passed through ENVI-carb cartridges to eliminate matrix. Then, the purified extracts were evaporated using nitrogen gas, and reconstituted into HPLC-MS/MS mobile phase to 0.4 mL. Extraction procedure for activated carbon air cleaner is concluded in **Fig. 4.4**.

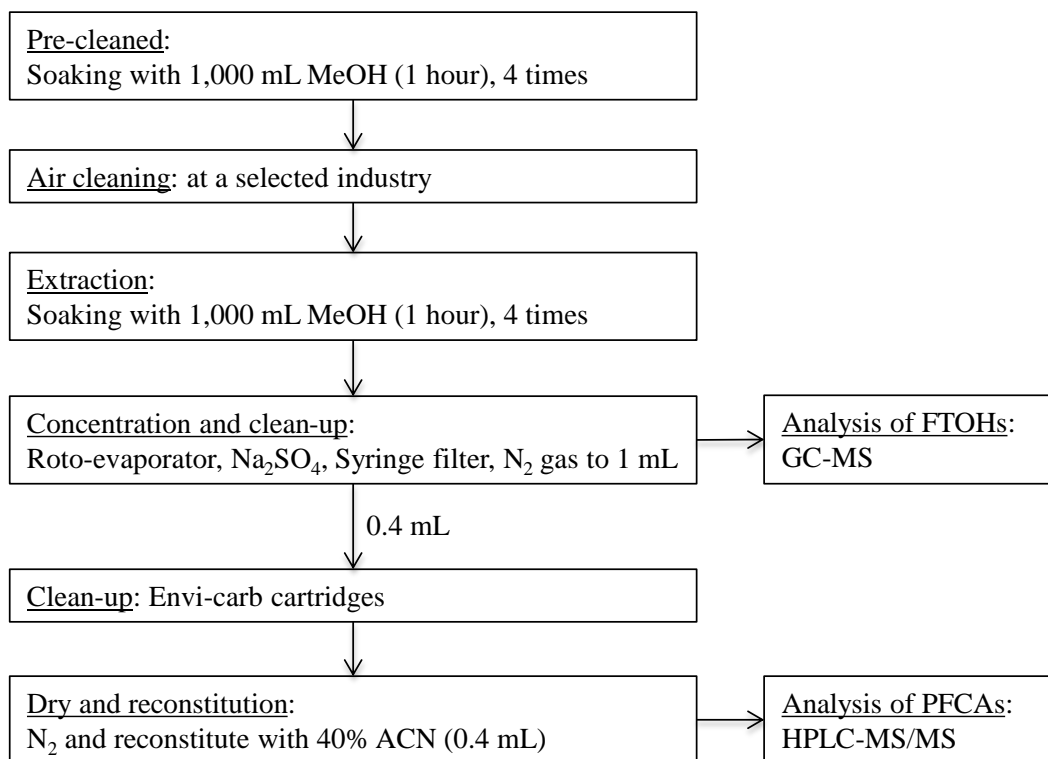


Figure 4.4 Analytical procedures for FTOHs and PFCAs in activated carbon fiber filter of air cleaner

4.3.6 Instrumental Analysis

6:2 FTOH, 8:2 FTOH and 10:2 FTOH were quantified by Agilent 6890 gas chromatography (GC)/Agilent 5973 mass spectrometer (MS) in electron ionization mode using selective ion monitoring. The purified extracts (2 μL) were injected to GC-MS with splitless mode at temperature of 230°C. The target compounds were separated on 30 m DB-WAX capillary column with 0.25 mm inner diameter and 0.25 μm film thickness. Helium was used as a carrier gas at a constant flow of 1 mL/min. GC oven was set at 50°C for 5 min, increased to 240°C with a ratio of 10°C/min (19 min) and held at 240°C for 1 min, resulting in total run time of 25 min. Ion source and quadrupole temperatures were 230 °C and 150°C, respectively. The analytical parameters for FTOHs *i.e.* quantifier and qualifier ions and retention time (*RT*) are shown in **Table 4.3**.

Table 4.3 Analytical parameters for analysis by GC-MS and HPLC-MS/MS

Compounds	Ion1 (<i>m/z</i>)	Ion2 (<i>m/z</i>)	<i>RT</i> (min)	<i>IDLs</i> (pg/ μL)	<i>IQLs</i> (pg/ μL)	<i>MDLs</i> (pg/ m^3)	<i>SQLs</i> (pg/ m^3)
GC-MS	Quantifier ion	Qualifier ion					
6:2 FTOH	344	363	9.6	3.5	11.5	4.8	16.0
8:2 FTOH	444	463	10.9	3.9	13.1	5.4	18.2
10:2 FTOH	505	563	12.2	4.3	14.5	6.0	20.1
¹³ C ₂ -8:2 FTOH	448	415	10.8	3.4	11.2	4.7	15.6
8:1 FA	363	431	11.0	4.1	13.6	5.7	18.9
HPLC-MS/MS	Parent ion	Daughter ion					
PFPeA	263	219	1.8	0.01	0.04	0.02	0.06
PFHxA	313	269	2.6	0.01	0.03	0.01	0.04
PFHpA	363	319	4.6	0.01	0.03	0.01	0.04
PFOA	413	369	7.1	0.01	0.04	0.02	0.06
PFNA	463	419	9.9	0.02	0.07	0.03	0.10
PFDA	513	469	12.5	0.01	0.03	0.01	0.04
PFUnDA	563	519	15.1	0.01	0.04	0.02	0.05
PFDoDA	613	569	17.7	0.01	0.04	0.02	0.06
¹³ C ₂ -PFHxA	315	271	2.8	0.02	0.04	0.03	0.06
¹³ C ₄ -PFOA	417	373	7.2	0.02	0.06	0.03	0.08
¹³ C ₂ -PFDA	515	471	12.7	0.02	0.06	0.03	0.08

PFCAs were analysed by Agilent 1200SL high performance liquid chromatography (HPLC) coupled with Agilent 6400 Triple Quadrupole mass spectrometer (MS/MS) in electrospray ionization negative mode using multiple reactions monitoring (MRM). The purified extracts (10 μ L) were injected to Agilent Eclipse XDB-C18 column (inner diameter 2.1 mm, length 100 mm and particle size 5 μ m). The mobile phase consisted of (A) 5 mM ammonium acetate in *ultrapure* water and (B) 100% acetonitrile. At a flow rate of 0.25 mL/min, separation process started with initial condition of 30% (B), increased to 50% (B) at 16.5 min, then to 70% (B) at 16.6 min and hold at 70% (B) for 3.4 min, after that went up to 90% (B) at 21 min and kept at 90% (B) for 1 min, and then ramped down to 30% (B), resulting a run time of 34 min. The analytical parameters for PFCAs *i.e.* quantifier and qualifier ions and retention time (RT) are shown in Table 4.3.

4.3.7 Quality Assurance and Control (QA/QC)

The concentrations were calculated using five points standard curve analysis for FTOHs (10-1,000 pg/ μ L), and PFCAs (0.1-10 pg/ μ L), in which the determination coefficients (R^2) were more than 0.99. Instrument detection limit (*IDL*) was defined as concentrations with signal to noise ratio (*S/N*) equal to 3:1. Instrument quantification limit (*IQL*) was used for quantifying analytes, which were defined by *S/N* 10:1. Method detection limit (*MDL*) and method quantification limit (*MQL*) were calculated from the *IDL* and *IQL*, respectively, when 720 m³ of air sample was collected. *MDLs* and *MQLs* of the target compounds were in the range 0.01-6.0 pg/m³ and 0.04-20.1 pg/m³, respectively (Table 4.3). 8:1 FA was added as an internal standard just prior to GC-MS analysis to correct sample volume variability. To confirm recovery of extraction and analysis method, mass-labeled standards were spiked to sampling media before extraction. Average recovery ¹³C₂-8:2 FTOH for gas and particle-phase was 78% and 77%, respectively (Table 4.4). The recovery of particle-phase of ¹³C₂-PFHxA, ¹³C₄-PFOA, ¹³C₂-PFDA was 127%, 84% and 104%, respectively. FTOHs and PFCAs in field blanks for Site C and Site D were below their *MDLs*, except some FTOHs and PFCAs for Site A, Site B, and during air cleaning in field experiment (Table 4.5), which their results were corrected by blank values.

Table 4.4 Recoveries of mass-labeled standards in air samples

List	Gas-phase (<i>n</i> =7)	Particle-phase (<i>n</i> =7)			
	¹³ C ₂ -8:2 FTOH	¹³ C ₂ -8:2 FTOH	¹³ C ₂ -PFHxA	¹³ C ₄ -PFOA	¹³ C ₂ -PFDA
Range	50-101	72-82	104-148	72-105	67-114
Average± <i>S.D.</i>	78±15	77±4	127±14	84±10	104±17

Table 4.5 FTOHs and PFCAs in field blanks

Sites	Concentration (pg/μL)										
	6:2 FTOH*	8:2 FTOH*	10:2 FTOH*	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
Site A	24, 16	12, <i>n.d.</i>	<i>n.d.</i> , <i>nd.</i>	<i>n.d.</i>	4.36	<i>n.d.</i>	0.34	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
Site B	<i>n.d.</i> , <i>n.d.</i>	25, <i>n.d.</i>	17, <i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
Site C	<i>n.d.</i> , <i>n.d.</i>	<i>n.d.</i> , <i>n.d.</i>	<i>n.d.</i> , <i>nd.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
Site D	<i>n.d.</i> , <i>nd.</i>	<i>n.d.</i> , <i>n.d.</i>	<i>n.d.</i> , <i>nd.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
AS-gas	9	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.56	0.16	0.21	0.33	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
AS-particle	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.25	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
AC	<i>n.d.</i>	55	27	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.03	<i>n.d.</i>	<i>n.d.</i>	0.13	<i>n.d.</i>

Note: *the values were for gas-phase, particle-phase of FTOHs, AS = air samples during air cleaning, AC = activated carbon fiber of air cleaner

4.4 Results and Discussion

4.4.1 Spatial Contamination of Airborne FTOHs and PFCAs

FTOHs and PFCAs were detected at every sampling site in Japan. Most of the target compounds were detected 100% in air samples, except for 6:2 FTOH, PFUnDA and PFDoDA which were detected 80% of the samples. Concentrations of target compounds at each sampling site in Japan are detailed in **Appendix I**. Average total concentration of three FTOHs (Σ FTOH) and eight PFCAs (Σ PFCA) for four sampling sites are shown in **Fig. 4.5**. The highest concentration of both Σ FTOH (588,000 pg/m³) and Σ PFCA (604,000 pg/m³) were detected in the fluorotelomer compounds production industry (Site A) and the second highest of Σ FTOH (219,000 pg/m³) and Σ PFCA (7,100 pg/m³) were detected in the industry which using fluorotelomer compounds for their production process (Site B). Much lower concentration of Σ FTOH (1,800 pg/m³) and Σ PFCA (140 pg/m³) were detected at the near-source site (Site C). At a remote site (Site D), Σ FTOH (130 pg/m³) and Σ PFCA (25 pg/m³) was about four to five order of magnitudes lower than those in the industries. These results indicated that industries was important emission sources of FTOHs and PFCAs to atmosphere in the study area.

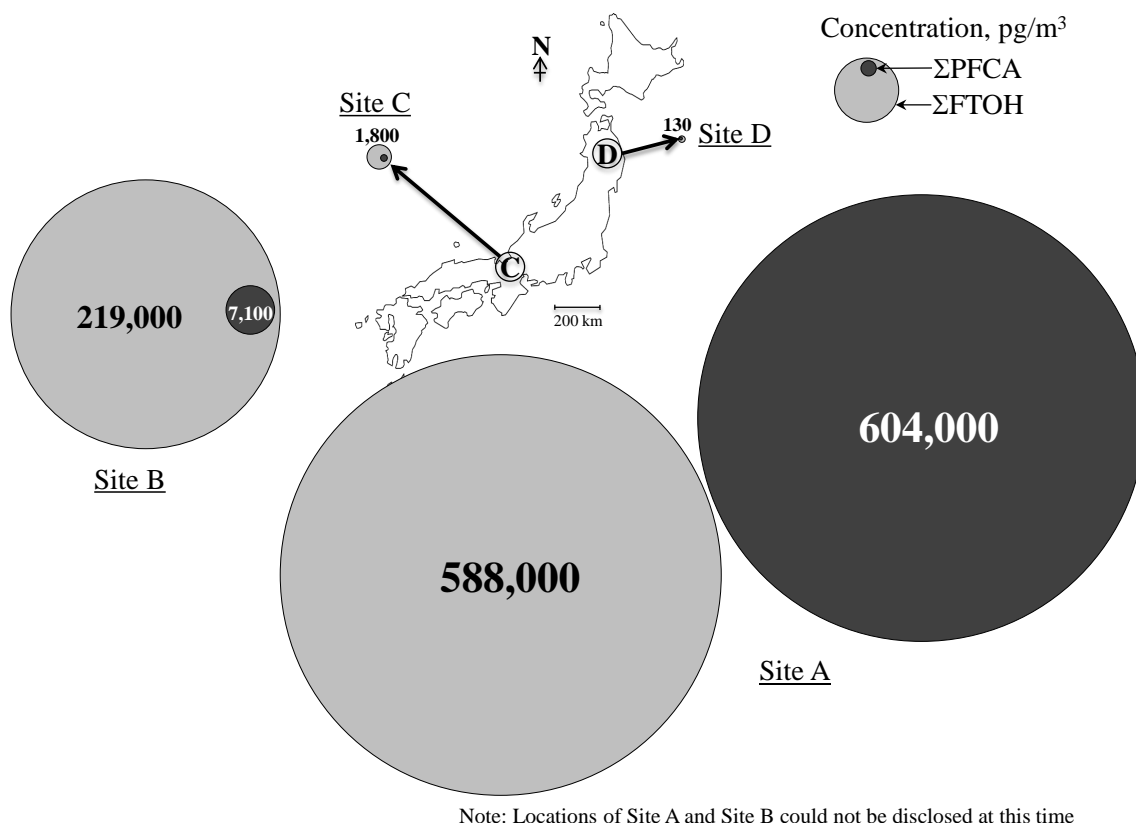


Figure 4.5 Spatial contamination of FTOHs and PFCAs in study areas in Japan

Concentrations of each FTOH and PFCA at each sampling point are shown in **Fig. 4.6**. Different FTOHs and PFCAs compounds were emitted from the industrial sources. 6:2 FTOH ($>400,000 \text{ pg/m}^3$) and PFHxA ($>600,000 \text{ pg/m}^3$) with very high concentrations were emitted from the fluorotelomer compounds production industry (Site A) whereas 8:2 FTOH ($>200,000 \text{ pg/m}^3$) and 10:2 FTOH ($>100,000 \text{ pg/m}^3$) were emitted from the industry which using fluorotelomer compounds for their production process (Site B). High concentration of these compounds at the process room and WWTP inferred that FTOHs and PFCAs can be directly evaporated during industrial production and also from contaminated wastewater. Lower concentrations of 8:2 FTOH and 10:2 FTOH were detected at roof top of a building of Site 3 (Site B (3)), compared to those in the process room (Site B (1)) and WWTP (Site B (2)). After emission from the sources, the compounds were transported in the air by wind and diluted with surrounded air. At the near-source site (Site C) and remote site (Site D), FTOHs and PFCAs were detected at very low concentrations compared to the industrial sources.

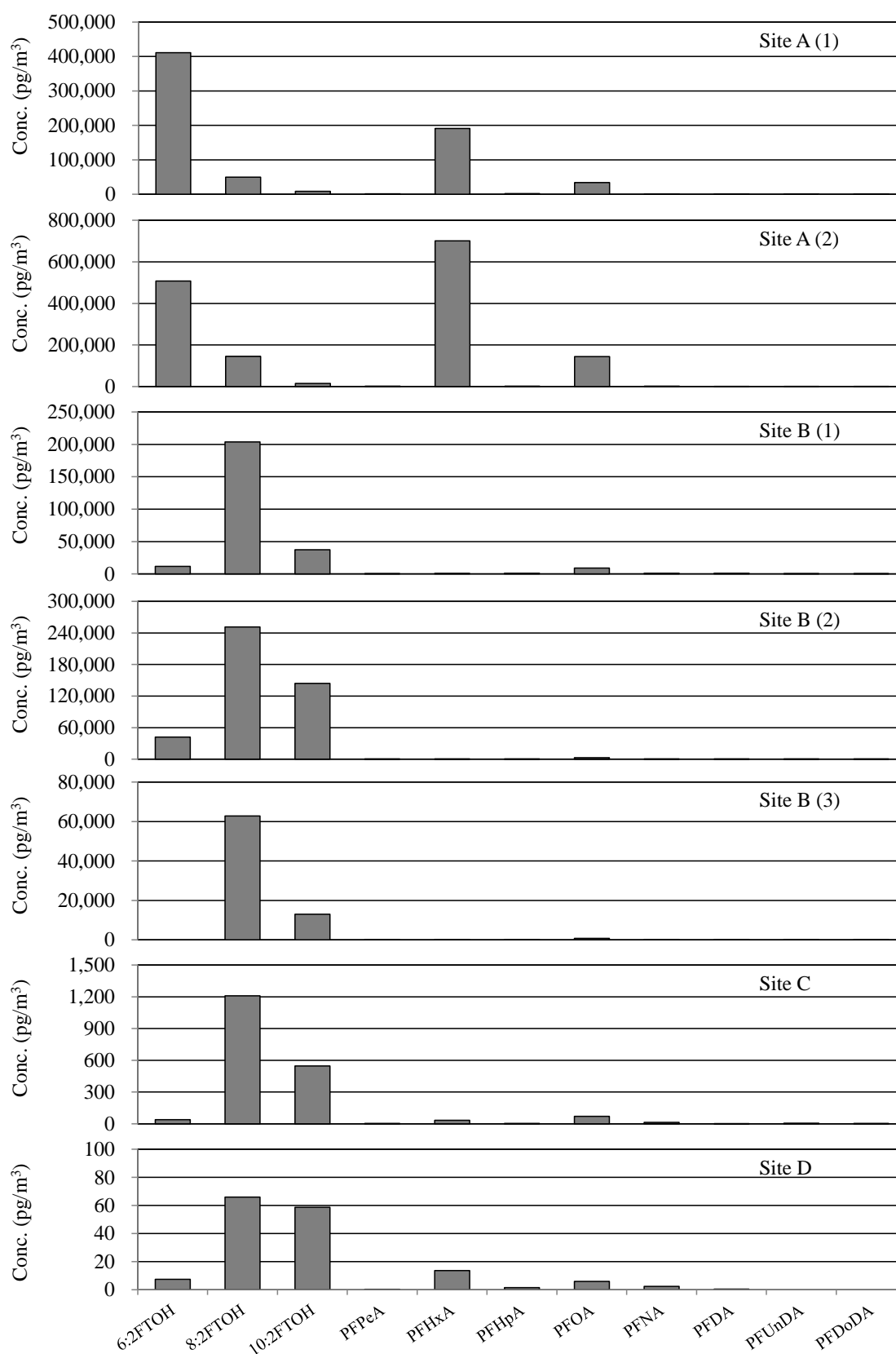


Figure 4.6 Concentration levels of FTOHs and PFCAs at each sampling point

4.4.2 Comparison with other Studies

Comparison of FTOHs concentrations in air in this study and previous studies in Japan is shown in **Fig. 4.7**. Oono et al., (2008a, 2008b) reported national wide-scale of FTOHs contamination across Japan (*n.d.*-2,560 pg/m^3). The concentrations at near-source site (1,800 pg/m^3) and remote site (130 pg/m^3) in this study were consistent with the mentioned previous studies. However, FTOHs concentrations at the fluorotelomer compounds production industry (588,000 pg/m^3) and the industry which using fluorotelomer compounds for their production process (219,000 pg/m^3) in this study indicated an important data for emission sources of FTOHs from industrial sectors to atmosphere. Compared to previous studies (Fig. 3.5 and Fig. 3.6), the results at the industrial sources in this study showed the highest concentrations of FTOHs which have been detected in air environment.

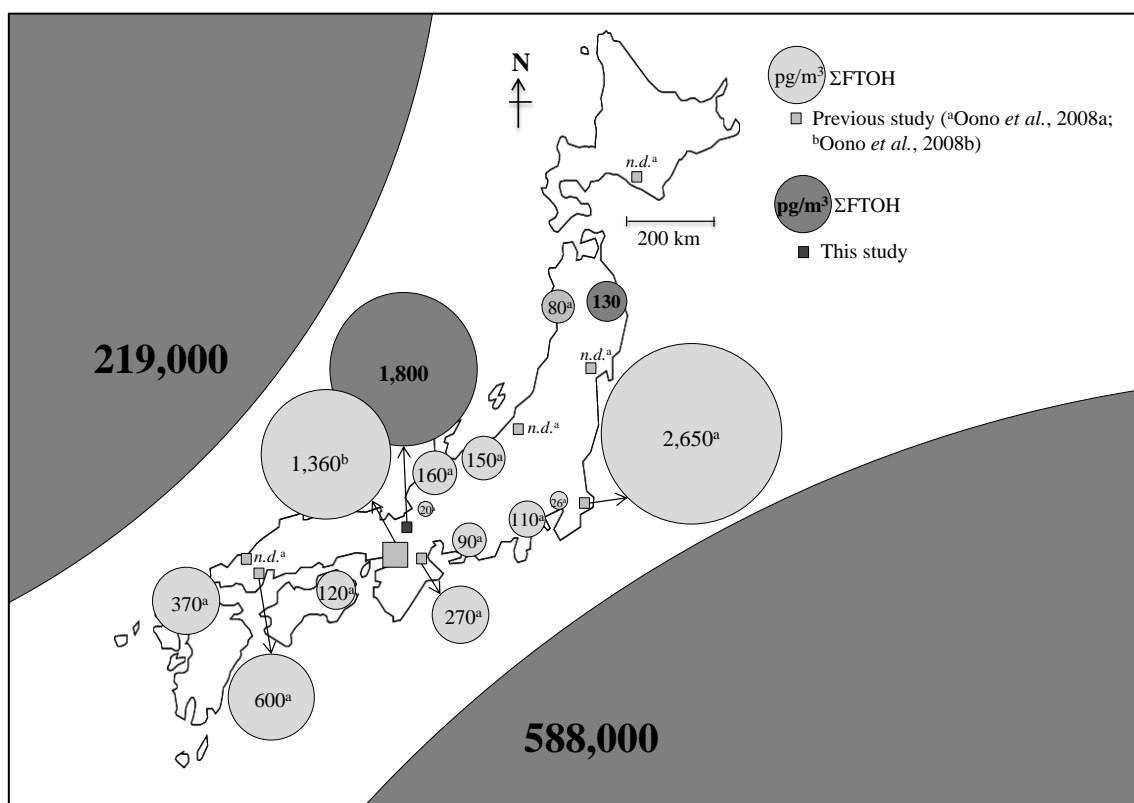


Figure 4.7 Comparison of FTOHs concentrations in Japan in this study and previous studies

In previous study (Harada *et al.*, 2005), PFOA were detected at a busy traffic route in Kyoto and at a local road in Iwate prefecture with the concentration of 70-920 pg/m³ and 1.6-2.6 pg/m³, respectively. Compared with this study that very high PFOA (145,000 pg/m³) were detected in the fluorotelomer compounds production industry. Thus, the results in this study showed that not only FTOHs but also PFCAs were released with very high concentrations from industries to air environment in Japan.

4.4.3 Composition Profiles and Phase Partitioning

4.4.3.1 Composition Profiles

Figure 4.8 shows composition profiles of FTOHs and PFCAs in the sampling sites in Japan. 6:2 FTOH was the dominant compound at Site A (80%), whereas 8:2 FTOH was the dominant compound among FTOHs at Site B (69%), Site C (67%) and Site D (50%). For PFCAs, PFHxA was the dominant compound at Site A (82%) and Site D (55%), and PFOA was the dominant compound at Site B (63%) and Site C (51%). Similar composition profiles of FTOHs and PFCAs at Site B and Site C indicated that contaminations of these pollutants in air of the near-source site (Site C) might be affected by the industry which using fluorotelomer compounds for their production process (Site B). However, the concentrations at each location can be affected by several sources and other influencing factors such as atmospheric lifetime and removal, physicochemical properties of each pollutant and meteorological conditions. PFCAs proportion was high at the fluorotelomer compounds production industry (Site A=51%), whereas its proportion was low at the other sites (Site B=3%, site C=7% and Site D=16%). Wet deposition was suggested as an effective atmospheric removal mechanism of PFCAs (Kwok *et al.*, 2010; Taniyasu *et al.*, 2013a), whereas FTOHs were difficult to be wet deposited from the air because they have relatively high vapor pressure and low water solubility (Gauthier and Mabury, 2005; Loewen *et al.*, 2005), compared to PFCAs. These reasons may explain dominance of FTOHs, rather than PFCAs (**Fig. 4.6**), at the near-source site (Site C) and the remote site (Site D).

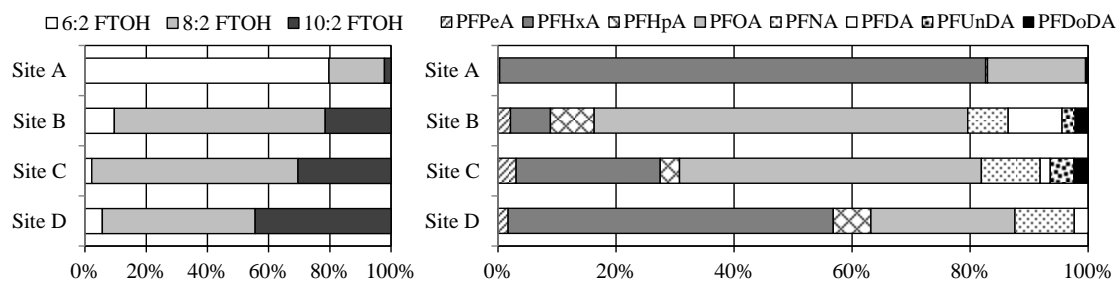


Figure 4.8 Composition profiles of FTOHs and PFCAs in study sites in Japan

4.4.3.2 Phase Partitioning

Figure 4.9 shows gas and particle-phase partitioning of FTOHs for fifteen air samples at four sampling sites. FTOHs were dominant in gas-phase fractions (69-100%); however, their detection in particle-phase increased with increasing of carbon chain length. As a result, the highest proportion of particle phase 6:2 FTOH, 8:2 FTOH and 10:2 FTOH was 5%, 7% and 31%, respectively.

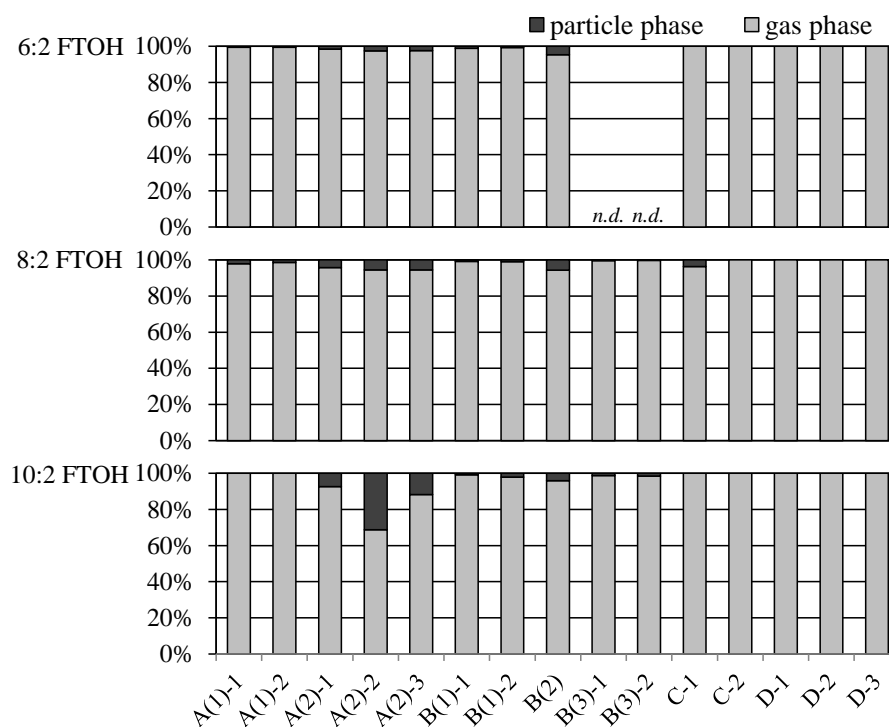


Figure 4.9 Gas- and particle-phase partitioning of FTOHs

Figure 4.10 shows particle and gas-phase partitioning of airborne FTOHs and PFCAs during air cleaning at the fluorotelomer compounds production industry. FTOHs were dominant in gas-phase fraction, which detection of 6:2 FTOH, 8:2 FTOH and 10:2 FTOH in gas-phase ranged 86.6%, 77.9% and 100%, respectively. On the other hand, PFCAs were mainly detected in particle-phase (73.4-99.8%).

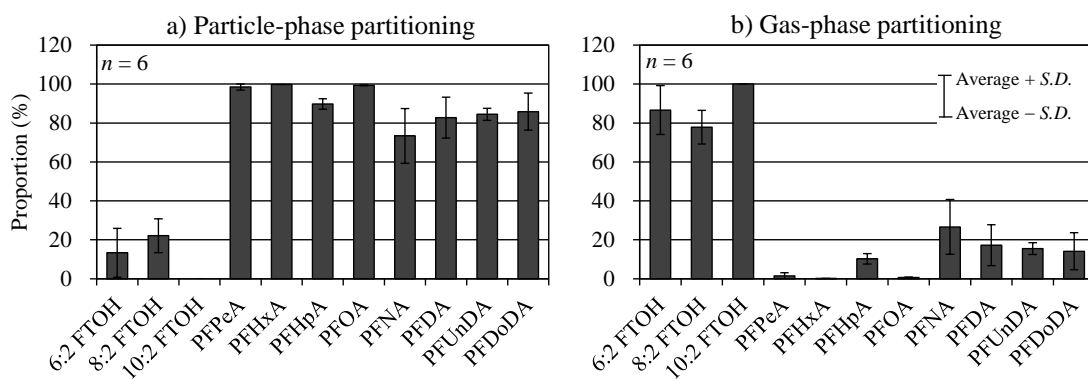


Figure 4.10 Particle- and gas-phase partitioning of FTOHs and PFCAs during air cleaning at the fluorotelomer compounds production industry

Figure 4.11 shows scatter plots between particle-phase FTOHs and total particulate matter (TPM) and **Fig. 4.12** shows the plots between particle-phase PFCAs and TPM. TPM was determined by weighting GFFs before and after air sampling in this study. Relationship between particle-phase FTOHs/ PFCAs and TPM were analyzed using Pearson correlation. FTOHs and PFCAs concentrations below *MDLs* were not assigned for statistical analysis.

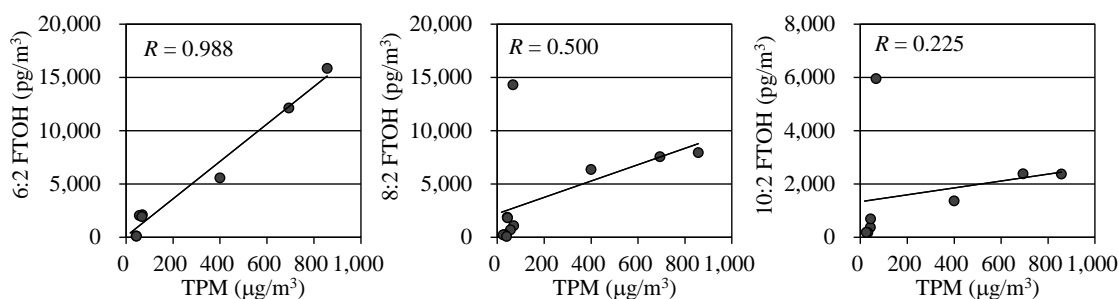


Figure 4.11 Correlations between particle-phase FTOHs and TPM

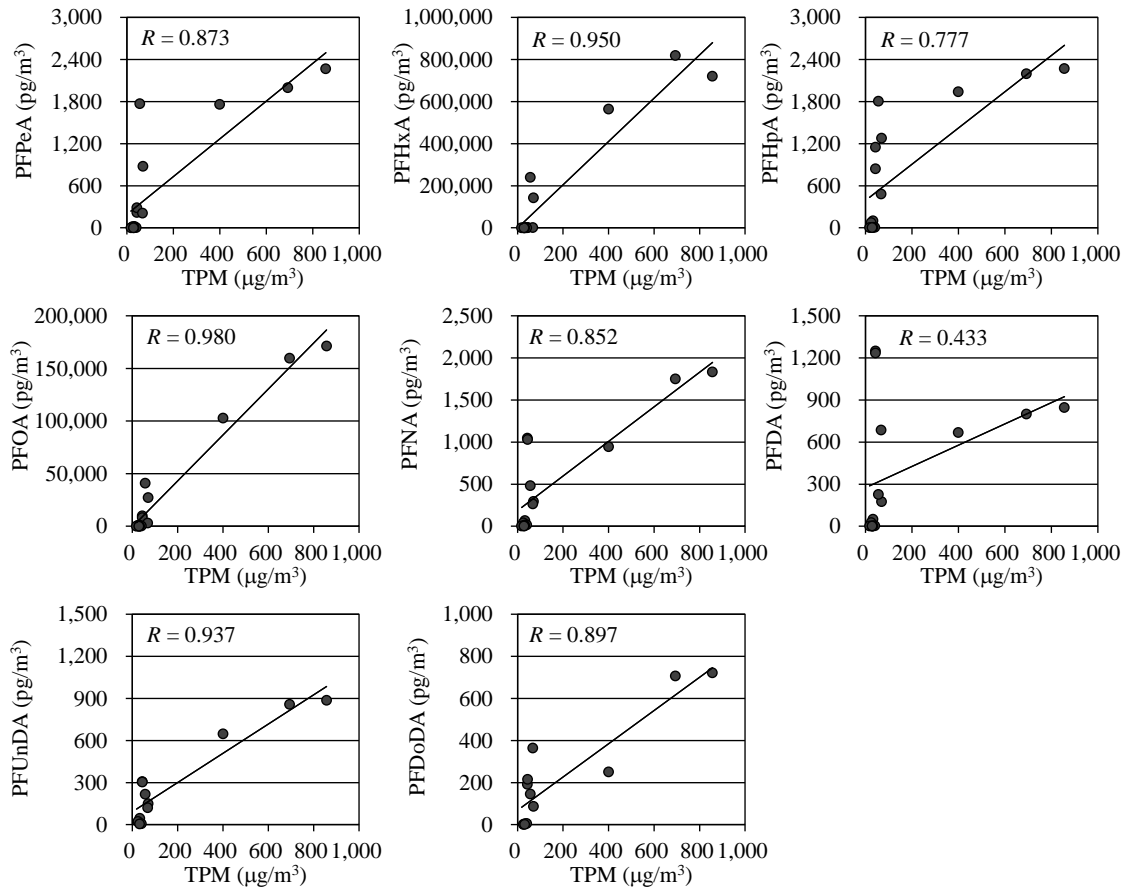


Figure 4.12 Correlations between particle-phase PFCAs and TPM

Strong correlations ($R > 0.7$) were found for 6:2 FTOH and most of PFCAs. This results indicated that particle mass was a governing factor on their particle-phase fractions. High concentration of these pollutants at the industrial sources inferred enrichment of the compounds onto particulate matter. Moderate correlations with TPM were found for 8:2 FTOH ($R = 0.500$) and PFDA ($R = 0.433$) and weak correlations for 10:2 FTOH ($R = 0.225$) which showed that the fractions might be also influenced by other factors such as chemical compositions and sources of particle, and meteorological conditions.

4.4.4 Inhalation Intakes of FTOHs and PFCAs

Inhalation intakes of FTOHs and PFCAs in Japan were calculated using eq. 4.1.

$$I_{air} = \frac{C_{air} \times Q_{air} \times F_{uptake}}{BW} \quad \text{eq.} \quad 4.1$$

where I_{hal} is an inhalation intake (ng/kg-day). C_{air} is concentrations of FTOHs/ PFCAs in air (ng/m³). Average concentrations of FTOHs and PFCAs at each sampling site were used for mean scenario and their highest concentrations were used for the worst scenario. Q_{air} is an volume inhaled rate (14.6 m³/day for mean scenario and 24 m³/day for worst scenario). F_{uptake} is an uptake fraction of the compounds (0.38 and 0.8 for mean scenario of FTOHs and PFCAs, respectively and 1 for the worst scenario of all compounds). BW is a body weight which was assumed of 50 kg for the calculation. The intakes in Japan were calculated only for adults.

Table 4.6 shows inhalation intakes of FTOHs and PFCAs from different locations in Japan. Very high intake rates of both airborne FTOHs and PFCAs were found in a contaminated site at the fluorotelomer compounds production industry and their rates in worst scenario (402 ng/kg-day for FTOHs and 474 ng/kg-day for PFCAs) were higher than the recommendation value (300 ng/kg-day). Lower intake rates were obtained for the exposure in another contaminated site at industry which using fluorotelomer compounds for their production process; however, intake of FTOHs in the worst case scenario was quite high (210 ng/kg-day). Much lower intake rates were obtained for the near-source site and the remote site, compared to the contaminated sites.

Table 4.6 Inhalation intakes of FTOHs and PFCAs in Japan

Sampling sites	Compounds	Inhalation Intakes (ng/kg-day)	
		Mean scenario	Worst scenario
Fluorotelomer compounds production industry	FTOHs	65	402
	PFCAs	141	474
	PFOA	23	82
Industry which using fluorotelomer compounds for their production process	FTOHs	24	210
	PFCAs	1.7	6.9
	PFOA	1.1	4.7
Near-source site	FTOHs	0.20	1.35
	PFCAs	0.03	0.09
	PFOA	0.02	0.06
Remote site	FTOHs	0.015	0.075
	PFCAs	0.006	0.014
	PFOA	0.001	0.003
Japanese Government recommendation	PFOA	300	

4.4.5 Removal of Airborne FTOHs and PFCAs

Figure 4.13 shows concentrations of FTOHs and PFCAs in air at the fluorotelomer compounds production industry during air cleaning experiment. First two air samples (AS1 and AS2) showed the concentrations before the cleaning and the last four air samples (AS3-AS6) showed the concentrations after the cleaning. FTOHs and PFCAs in air were gradually decreased during the cleaning process. Average concentration of all target compounds (three FTOHs and eight PFCAs) before and after the cleaning was 710,540 and 382,350 pg/m^3 , respectively. Figure 4.14 shows reduction of each target compound. Reduction rates of FTOHs (48-88%) were higher than that of PFCAs (3-53%) and long chain PFCAs (C8-C12) have no trend of reduction during air cleaning process. This might be due to higher emission rate of PFCAs and activated carbon air cleaner might have more effective for FTOHs, compared to PFCAs.

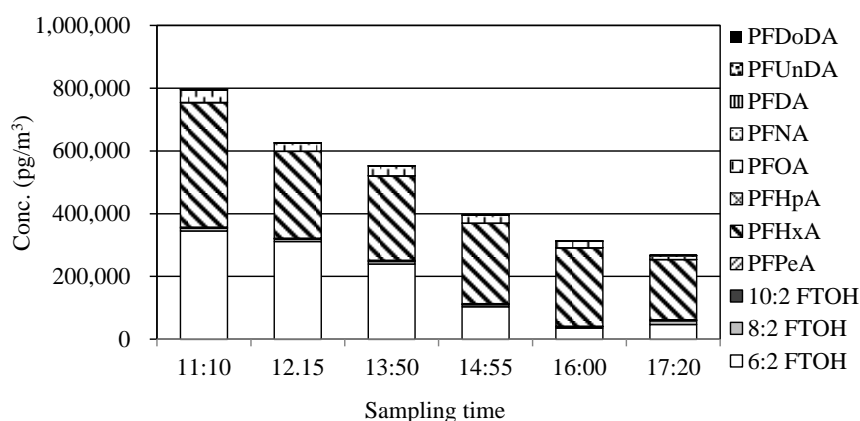


Figure 4.13 Concentrations of FTOHs and PFCAs during air cleaning

Absorption of target compounds (FTOHs and PFCAs) onto activated carbon fiber (ACF) filter of air cleaner was checked to confirm their removal by this air cleaning experiment. Recoveries of target compounds for four times of extraction (AC-R1 to R4) are shown in **Fig. 4.15**. High recovery (>96%) of all target compounds were obtained by the first three times of extraction process. Absorption amount of FTOHs and PFCAs onto activated carbon air cleaner are shown in **Fig. 4.16** and Appendix I. PFHxA and 6:2 FTOH were adsorbed at the highest amount, compared to other target compounds. Total amount of FTOHs and PFCAs adsorbed onto activated carbon of air cleaning was

225 μg , whereas the amount adsorbed on to XAD-2 resin of 6 hours air sampling (30 m^3/hour) was 88 μg . Reduction of target compound in the sludge thickener building and adsorbed FTOHs/ PFCAs onto activated carbon air cleaner inferred that the air cleaner can be applied for air cleaning in this industry. However, higher cleaning rate and enclosing the building are needed for higher removal rates.

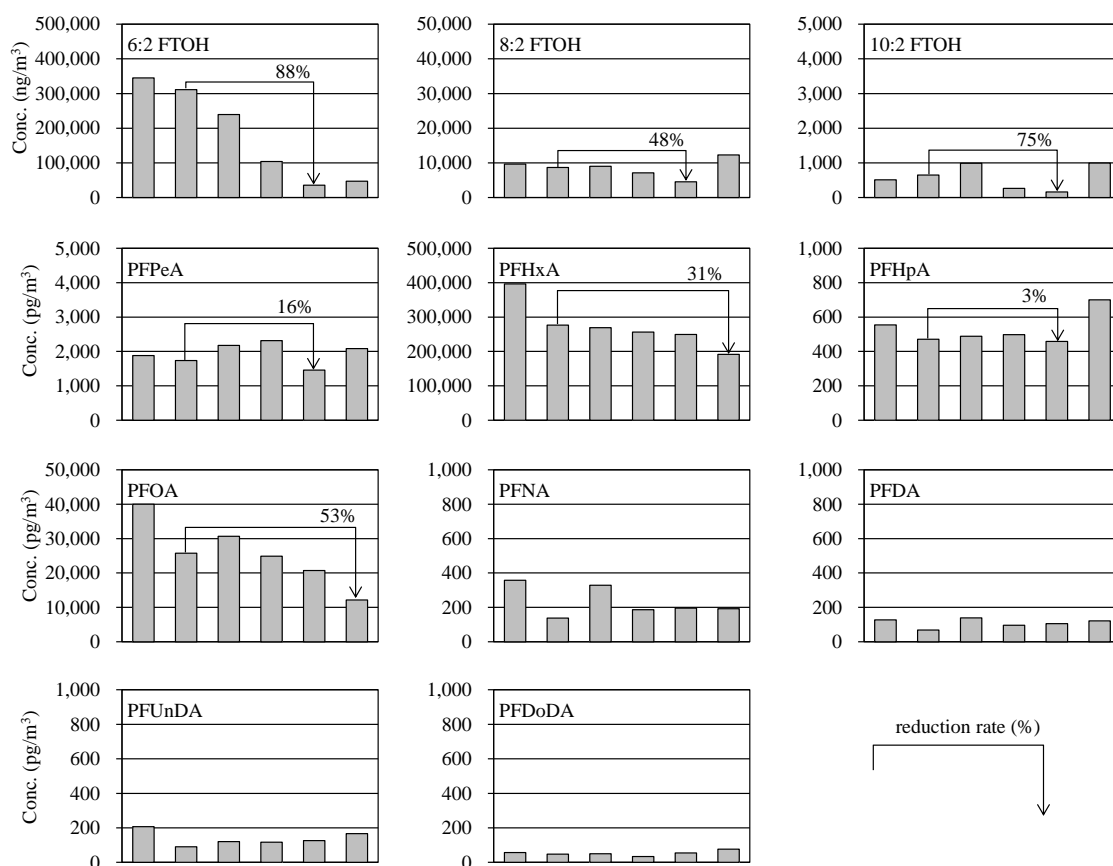


Figure 4.14 Reduction of FTOHs and PFCAs during air cleaning in field experiment

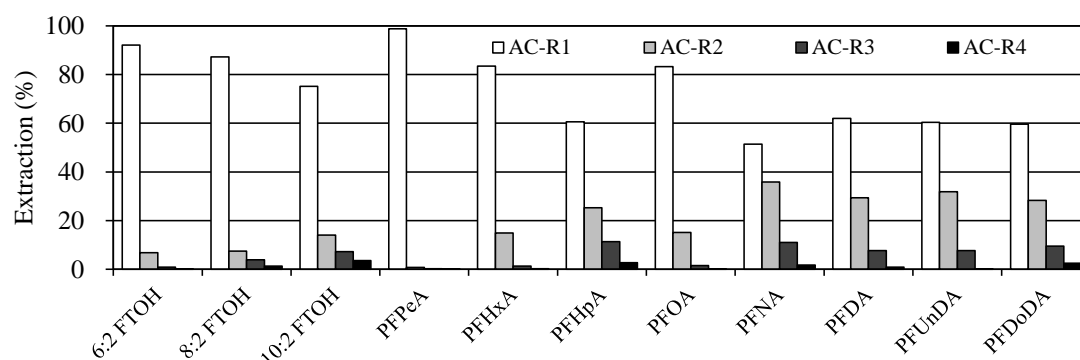


Figure 4.15 Extraction recoveries of FTOHs and PFCAs by extraction process for activated carbon air cleaner

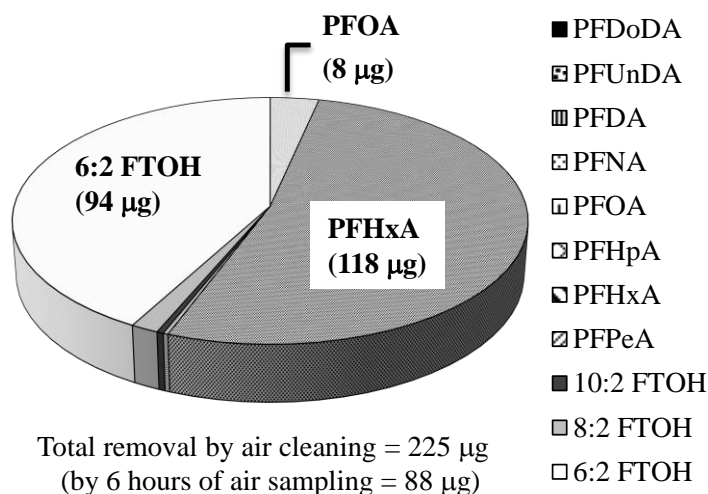


Figure 4.16 Amount of FTOHs and PFCAs adsorbed onto activated carbon air cleaner

4.5 Summary

Very high concentrations of FTOHs and PFCAs in air were detected in the fluorotelomer compounds production industry ($588,000 \text{ pg/m}^3$ and $604,000 \text{ pg/m}^3$, respectively) in Japan. High concentrations of FTOHs ($219,000 \text{ pg/m}^3$) were also detected in the industry which using fluorotelomer compounds for their production process. Much lower concentrations of FTOHs and PFCAs were detected at the near-source site ($1,800 \text{ pg/m}^3$ and 140 pg/m^3 , respectively). Four to five levels of magnitude of airborne FTOHs and PFCAs in this industry were higher than those in a remote site (130 pg/m^3 and 25 pg/m^3 , respectively). These results indicated industrial emission point sources of FTOHs and PFCAs to atmosphere of the study areas in Japan. Compared to previous studies in Japan and other countries, this study showed the highest concentration of FTOHs and PFCAs which have been detected in air environment.

Different FTOHs/ PFCAs compounds were emitted from the industrial sources. 6:2 FTOH and PFHxA were the dominant compounds from the fluorotelomer compounds production industry whereas 8:2 FTOH and 10:2 FTOH were the dominant compounds from the industry which using fluorotelomer compounds for their production process. High concentration of these compounds at the process room and WWTPs confirmed that

FTOHs and PFCAs were evaporated from industrial production processes and contaminated wastewater. Similar composition profiles of FTOHs and PFCAs at the industry which using fluorotelomer compounds for their production process and the near-source site indicated that the contaminations of these pollutants in the air of the near-source site might be affected by this industry.

FTOHs were dominant in gas-phase (77.9-100%) whereas PFCAs were mainly detected in particle-phase (73.4-99.8%). Proportion of PFCAs/FTOHs was high at the fluorotelomer compounds production industry (51%), whereas its proportion was low at the other sites; the industry which using fluorotelomer compounds for their production process (3%), the near-source site (7%) and the remote site (16%). This may explain by wet deposition mechanism, which was effective for PFCAs removal from the air whereas it was negligible for FTOHs. Strong correlations were found between total particulate matter (TPM) and particle-phase 6:2 FTOH, and between TPM and most of particle-phase PFCAs. These results indicated their enrichment onto particulate matter from industrial sources.

In Japan, very high inhalation intakes of FTOHs and PFCAs were found at the fluorotelomer compounds production industry. Total intake of FTOHs and PFCAs was 206 ng/kg-day for mean scenario and 876 ng/kg-day for worst scenario, which exceeded recommendation guideline by Japanese government (300 ng/kg-day). Air cleaning in field experiment was conducted in this industry in the sludge thickener building. FTOHs and PFCAs were removed from the air using activated carbon air cleaner. Higher reduction rates were observed for FTOHs (48-88%), compared to PFCAs (3-53%). To obtain higher efficiency, enclosing the building and higher cleaning rate are needed.

Chapter 5

Distribution Pathways of Airborne PFCAs and FTOHs by Wet Deposition and Photodegradation

5.1 Introduction

Perfluoroalkyl carboxylates (PFCAs) have been considered as emerging pollutants due to their persistent, bio-accumulative and toxic properties (Lau *et al.*, 2007; Andersen *et al.*, 2008). While monitoring studies have clearly shown contamination of PFCAs in the environment but their sources and transport pathways remain unclear.

PFCAs can be directly emitted to the environment after productions and uses. They are highly soluble in water, moderate sorption to solid but less volatile (Prevedouros *et al.*, 2006; Conder, *et al.*, 2007), and aquatic environment has been recognized as a dominant compartment for transportation and sinks of PFCAs (Ahrens, 2013). However, PFCAs were detected in the air, bound onto particulate matter. In addition, atmospheric transportation and degradation of their precursor compounds *i.e.* fluorotelomer alcohols (FTOHs) were suggested as an indirect source of PFCAs in the environment (Ellis *et al.*, 2004; Dreyer *et al.*, 2009). Therefore, the atmosphere might play an important role as an environmental sink and secondary source of PFCAs. Wet deposition was suggested as an effective atmospheric removal and one of the contamination sources of PFCAs in river water (Know *et al.*, 2010; Taniyasu *et al.*, 2013a). PFCAs are persistent and difficult to degrade under natural environmental conditions, while FTOHs are considered as degradable compounds. Solar radiation induced by photolysis is suggested as the primary route for degradation of many anthropogenic chemicals (Vaalgamaa *et al.*, 2011) but very little is currently known for FTOHs.

Therefore, this chapter investigated distribution of PFCAs and FTOHs from the air to water environment *via* wet deposition and photodegradation. Understanding this distribution could provide further evidence on their transport pathways in the environment.

5.2 Objectives

This chapter aims (1) to investigate concentrations and profiles of PFCAs and FTOHs in rainwater samples, (2) to calculate their fluxes from air to water environment *via* wet deposition, (3) to compare the concentrations and fluxes with previous studies, (4) to examine changes of PFCAs and FTOHs by a sunlight exposure experiment, and (5) to propose distribution pathways of these target compounds by wet deposition and photodegradation in the environment

5.3 Methodology

5.3.1 Locations and Sample Collection

5.3.1.1 Rainwater Collection

Combination of a polyethylene funnel (ϕ 30 cm, Sogorikagaku glass work, Kyoto, Japan) and a bottle (6 L of volume capacity) was used as a rainwater sampler. The location of sampling was on the rooftop (approximately 12 m above the ground) of a four-story reinforced concrete building in Kyoto University and the funnel's mouth was kept at approximately 1.0 meter height above the floor to avoid splashes of rain into the bottles. Three sets of samplers were always installed there just a few hours before each rainfall started, and they were removed immediately after the rain ended to avoid dry deposition collection. Total surface area of three samplers was 0.212 m². Rainwater sampling was conducted at seven rainfall events during May to October 2013. **Table 5.1** shows collection date, rainfall duration, precipitation amount, antecedent dry weather period and cumulative sunshine duration before each rainfall event, and rainwater characteristics (pH, conductivity and temperature). There was a heavy rain during September 15-16, 2013 (Rain 6) with 250.5 mm of precipitation. The collected rainwater in three samplers (0.212 m² surface area) was estimated to be 53.1 L which was over the maximum capacity of the sampling bottles (18 L). Therefore, two-third of rainwater overflowed from the sampling bottles during nighttime on those sampling days.

Table 5.1 Rainwater sample collection and characteristics

Rain	Collection date (2013)	Duration of rainfall (hours)	Precipitation amount (mm)	^{1/} Antecedent dry weather period (days)	^{1/} Cumulative sunshine duration (hours)	pH	Conductivity ($\mu\text{S}/\text{cm}$)	Temp. ($^{\circ}\text{C}$)
Rain (1)	May 28-29	22	16.5	9	74.7	4.9	14	27.0
Rain (2)	June 19-20	23	79.9	4	16.1	4.9	5	25.0
Rain (3)	August 21	1	10.4	16	141.8	4.7	5	27.0
Rain (4)	August 23-24	19	8.1	2	8.6	4.6	12	28.0
Rain (5)	September 2-3	9	34.2	1	0.0	4.8	6	26.5
Rain (6) ^{2/}	September 15-16	32	250.5 ^{1/}	2	14.7	5.1	2	25.5
Rain (7)	October 23-24	11	11.7	3	6.4	5.0	4	23.0

Note: ^{1/} Data from Japan Meteorological Agency, October 2013 (<http://www.jma.go.jp/jma/index.html>)

^{2/} Rainwater overflowed from the sampling bottles

5.3.1.2 River Water Collection

Twelve liters of river water samples were collected from Chao Phraya River at Khlong Toei pier (**Fig. 5.1**), Bangkok, Thailand on December 21, 2013. Polypropylene (PP) bottles were used to collect the water. They were pre-washed by methanol and already dried before using. River water characteristics *i.e.* temperature (26.5°C), dissolve oxygen (2.2 mg/L), pH (6.8) and conductivity (7.4 mS/cm) were measured on the sampling day.

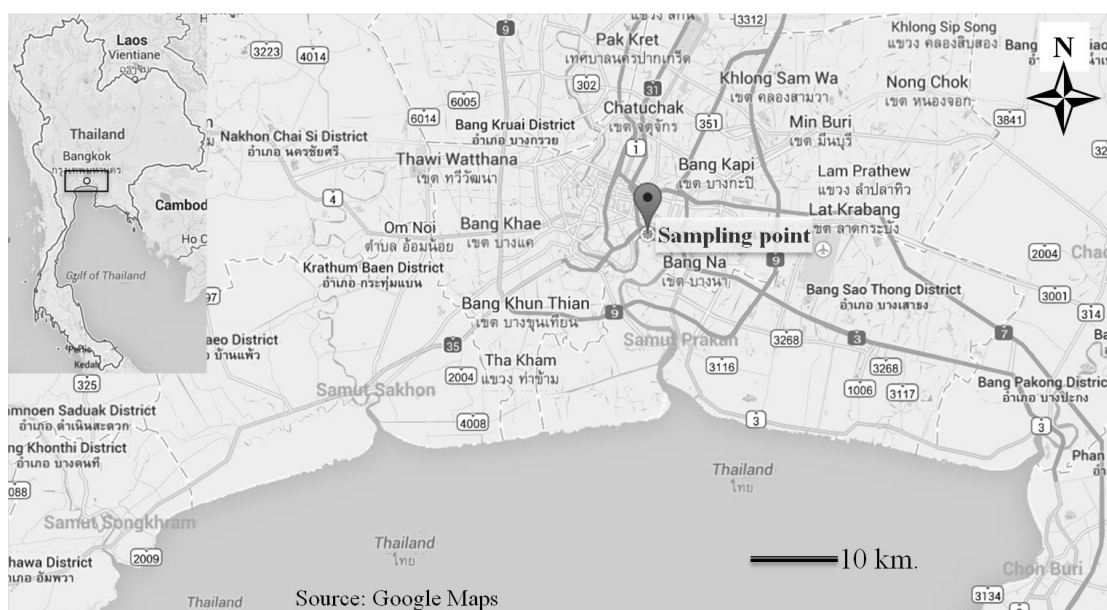


Figure 5.1 Sampling location of river water samples at Chao Phraya River, Thailand

5.3.2 Sunlight Exposure Experiment

A sunlight exposure experiment was conducted for three types of water samples; rainwater, 8:2 FTOH solution in *ultrapure* water and river water in order to examine changes of PFCAs and FTOHs in the water samples caused by sunlight. Conclusion of the sunlight exposure periods are shown in **Table 5.2**. Rain (1) and Rain (2) samples were put in PP bottles and placed on the rooftop of the building in Kyoto University, Japan. Rain (1) samples were exposed to sunlight during June 1-28, 2013, and they were collected twice after 1 week and after 4 weeks for analysis of PFCAs and FTOHs. Rain (2) samples were exposed to sunlight during June 22 to July 5, 2013, and they were collected twice after 1 week and after 2 weeks for the analysis.

The sunlight exposure experiment of 8:2 FTOH solutions was conducted to confirm its degradation and by-products formation by sunlight. Two sets of 8:2 FTOH solutions in *ultrapure* water (1,000 ng/L) were prepared and put in PP bottles. One set was placed on rooftop of the building in Kyoto University to expose to sunlight during July 26 to October 17, 2013. The samples were collected 4 times after 1 week, 2 weeks, 4 weeks, 8 weeks and 12 weeks of the exposure for 8:2 FTOH and PFCAs analysis. Another set was kept in dark condition as a control sample by wrapping the bottle with aluminum foil and keeping at 25°C in an incubator. After 12 weeks, 8:2 FTOH and PFCAs in the control sample were measured.

For river water samples, two sets of the samples were prepared; (1) no spike 8:2 FTOH and (2) spike 8:2 FTOH (1,000 ng/L) into river water samples. After that, the samples were exposed to sunlight at rooftop of a five-story reinforced concrete building in Mahidol University, Nakhon Pathom, Thailand during December 22, 2013 to January 18, 2014. They were collected 4 times after 1 week, 2 weeks, 3 weeks and 4 weeks of the exposure for PFCAs analysis.

Parameters influencing photodegradation *i.e.* water and air temperatures (°C), UV intensity (mJ/cm²) and illuminance (lux) were observed using thermometers, a UV detector (UVD-S254, USHIO, Tokyo, Japan, sensitive wavelength: 220-310 nm) and a

Digital Lux Meter (LX-204, Custom, Tokyo, Japan), respectively. These parameters were observed 24 times during daytime (6 am to 6 pm) basically on Saturday during Jun-Sep 2013 for the sunlight exposure experiment in Japan. The observation was also conducted 4 times during December 22, 2013 to January 18, 2014 for the sunlight exposure experiment in Thailand.

Sunlight absorption by the PP bottle's surface was examined by checking the UV intensity (mJ/cm^2) outside and inside the PP bottle. Most of the measurement results (>90%) were not different between them, so the bottle's absorption was considered to be negligible.

Table 5.2 Conclusion of sunlight exposure periods for water samples

Sunlight exposure	Rain (1)	Rain (2)	8:2 FTOH in <i>Ultrapure</i> water	River water
1 week	Jun 1-7, 2013	Jun 22-28, 2013	Jul 26 to Aug 1, 2013	Dec 22-28, 2013
2 weeks	-	Jun 22 to Jul 5, 2013	Jul 26 to Aug 8, 2013	Dec 22, 2013 to Jan 4, 2014
3 weeks	-	-	-	Dec 22, 2013 to Jan 11, 2014
4 weeks	Jun 1-28, 2013	-	Jul 26 to Aug 22, 2013	Dec 22, 2013 to Jan 18, 2014
8 weeks	-	-	Jul 26 to Sep 19, 2013	-
12 weeks	-	-	Jul 26 to Oct 17, 2013	-

5.3.3 Chemicals and Standards

Eleven target compounds of three FTOHs (6:2 FTOH, 8:2 FTOH, 10:2 FTOH) and eight PFCAs (PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDODA) were purchased from Wako Pure Chemicals (Osaka, Japan). Four mass-labeled standard ($^{13}\text{C}_2$ 8:2 FTOH, $^{13}\text{C}_2$ -PFHxA, $^{13}\text{C}_4$ -PFOA and $^{13}\text{C}_2$ -PFDA) were purchased from the Wellington Laboratory Inc. (Ontario, Canada). Analytical or HPLC grade were used for all solvents and reagents. *Ultrapure* water was prepared by passing *Milli-Q* water through PrecepC-Agri (C18) cartridges (Wako, Japan) inline connected to Oasis[®]HLB cartridges (Waters, Japan) to remove any PFCAs from *Milli-Q* water.

5.3.4 Sample Preparation

Rainwater samples from seven rainfall events and the sunlight exposure experiment were pretreated for three portions of analysis; (1) liquid-phase PFCAs, (2) solid-phase PFCAs and (3) FTOHs (liquid- and solid-phase). A rainwater sample (500 mL) was filtered through a GF/B filter paper (1 μm , Whatman, GE Healthcare, Tokyo, Japan). All filtration materials and filter papers were pre-washed with methanol and dried before using. The filtrate was used for analysis of liquid-phase PFCAs and the particle onto the filter paper was used for solid-phase analysis of PFCAs. For FTOHs portion, the rainwater sample without filtration process was analyzed for both liquid- and solid-phase. Solution of 8:2 FTOH in *ultrapure* water was prepared for two portions of analysis; (1) liquid-phase PFCAs and (2) liquid-phase 8:2 FTOH. For river water, a sample (500 mL) was filtered and the filtrate was analyzed for liquid-phase PFCAs, whereas the filter paper was analyzed for solid-phase PFCAs. Analytical procedures of PFCAs and FTOHs for water samples are shown in **Fig. 5.2**. During the sample extraction and analysis, *ultrapure* water was used as a blank sample for the rainwater and river water analysis.

For extraction procedure of liquid-phase PFCAs (Kunacheva, 2009), the filtrate (500 mL) was loaded to PrecepC-Agri (C18) cartridge inline connected to Oasis[®] HLB cartridge using a Sep-Pak concentrator at a flow rate of 5 mL/min. Both cartridges were manually pre-conditioned by 10 mL of methanol and 20 mL of *ultrapure* water. The concentrator was pre-washed by methanol for 5 min at 5 mL/min followed by *ultrapure* water for 15 min at 5 mL/min before using. After sample loading, the cartridges were dried by a vacuum manifold (Nihon Waters K. K., Tokyo, Japan) for 2 hours. Target compounds in dried cartridges were eluted twice by 2 mL methanol, followed by 2 mL of acetonitrile. Then, the elute solution (6 mL) was evaporated until dried by nitrogen gas and reconstituted using HPLC-MS/MS mobile phase to 1 mL.

For a particle-phase sample, the filter paper was placed into 15 mL PP tube, 5 mL of methanol was added and shaken at 150 rpm for 1 hour. The extraction processes were conducted twice, and both extracted solutions were transferred into another PP tube. Later, the solution (10 mL) was passed through ENVI-Carb cartridge, which was

cleaned by methanol before using. Then, the eluted solution was dried by nitrogen gas and reconstituted for HPLC-MS/MS mobile phase. For determining the recovery of extraction and analytical procedures, mass-labeled PFCAs were spiked into the filtrated samples before loading to cartridges and onto the filter paper samples before extraction. Duplicate samples ($n=2$) were prepared and analysed for PFCAs in Rain (2), Rain (5), Rain (6), Rain (7), all solution of 8:2 FTOH in *ultrapure* water and all river water samples.

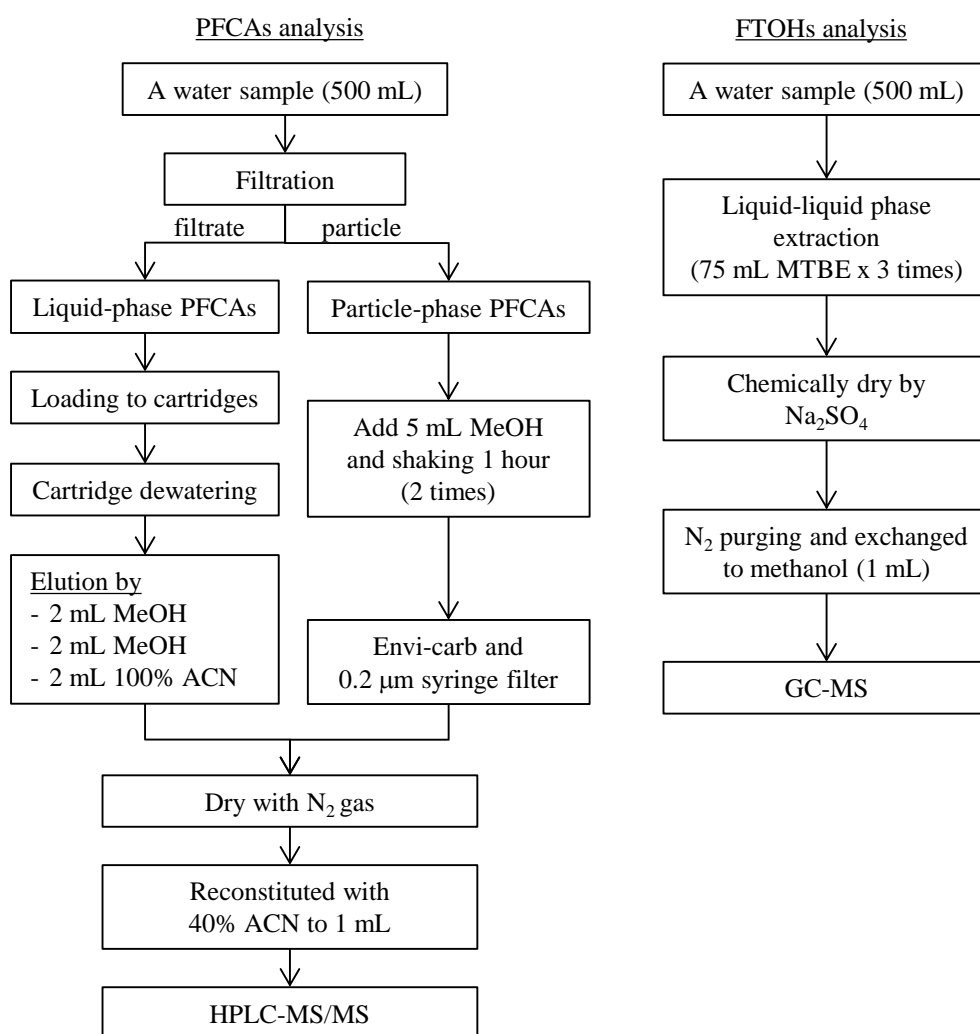


Figure 5.2 Analytical procedures of PFCAs and FTOHs for water samples

For the extraction procedure of FTOHs, 75 mL of methyl tetra butyl ether (MTBE) (Wako Pure Chemicals, Osaka, Japan) was added to a sample (500 mL) in a PP separation funnel and the sample was thoroughly shaken for 3 minutes. The dissolved

FTOHs in MTBE layer was collected into a PP bottle after discarding the bottom layer of water. The extraction processes were repeated 3 times (about 225 mL of extract in total). After that, the solvent was dried chemically by Na_2SO_4 , solvent exchanged to methanol and reduced to 1 mL using nitrogen gas.

5.3.5 Instrumental Analysis

PFCAs were analysed by Agilent 1200SL high performance liquid chromatography (HPLC) coupled with Agilent 6400 Triple Quadrupole mass spectrometer (MS/MS) in electrospray ionization negative mode using multiple reactions monitoring (MRM). The purified extracts (10 μL) were injected to Agilent Eclipse XDB-C18 column (inner diameter 2.1 mm, length 100 mm and particle size 5 μm). The mobile phase consisted of (A) 5 mM ammonium acetate in *ultrapure* water and (B) 100% acetonitrile. At a flow rate of 0.25 mL/min, separation process started with initial condition of 30% (B), increased to 50% (B) at 16.5 min, then to 70% (B) at 16.6 min and hold at 70% (B) for 3.4 min, after that went up to 90% (B) at 21 min and kept at 90% (B) for 1 min, and then ramped down to 30% (B), resulting a run time of 34 min. The analytical parameters for PFCAs *i.e.* parent ion, daughter ion and retention time (*RT*) are shown in **Table 5.3**.

6:2 FTOH, 8:2 FTOH and 10:2 FTOH were analysed by Agilent 6890 gas chromatography (GC)/ Agilent 5973 mass spectrometer (MS) in electron ionization mode using selective ion monitoring. The purified extracts (2 μL) were injected to GC-MS with splitless mode at a temperature of 230°C. The target compounds were separated on 30 m DB-WAX capillary column with 0.25 mm inner diameter and 0.25 μm film thickness. Helium was used as a carrier gas at a constant flow of 1 mL/min. The GC oven was set at 50°C for 5 min, increased to 240°C with a ratio of 10°C/min (19 min) and held at 240°C for 1 min, resulting in total run time of 25 min. Ion source and quadrupole temperatures were 230°C and 150°C, respectively. The analytical parameters for FTOHs *i.e.* quantification ion, qualification ion and retention time (*RT*) are also shown in Table 5.3.

Table 5.3 Analytical parameters for PFCAs (HPLC-MS/MS) and FTOHs (GC-MS)

Compounds	Ion 1 (<i>m/z</i>)	Ion 2 (<i>m/z</i>)	<i>RT</i> (min)	<i>IDLs</i> (ng/mL)	<i>IQLs</i> (ng/mL)	<i>MDLs</i> (ng/L)	<i>MQLs</i> (ng/L)
<u>HPLC-MS/MS</u>	<u>Parent ion</u>	<u>Daughter ion</u>					
PFPeA	263	219	1.8	0.01	0.04	0.03	0.09
PFHxA	313	269	2.6	0.01	0.03	0.02	0.05
PFHpA	363	319	4.6	0.01	0.03	0.02	0.06
PFOA	413	369	7.1	0.01	0.04	0.02	0.08
PFNA	463	419	9.9	0.02	0.07	0.04	0.15
PFDA	513	469	12.5	0.01	0.03	0.02	0.05
PFUnDA	563	519	15.1	0.01	0.04	0.02	0.07
PFDoDA	613	569	17.7	0.01	0.04	0.02	0.08
¹³ C ₂ -PFHxA	315	271	2.8	0.02	0.04	0.04	0.08
¹³ C ₄ -PFOA	417	373	7.2	0.02	0.06	0.04	0.12
¹³ C ₂ -PFDA	515	471	12.7	0.02	0.06	0.04	0.12
<u>GC-MS</u>	<u>Quantifier ion</u>	<u>Qualifier ion</u>					
6:2 FTOH	344	363	9.6	3.5	11.5	6.9	23.1
8:2 FTOH	444	463	10.9	3.9	13.1	7.8	26.1
10:2 FTOH	505	563	12.2	4.3	14.5	8.7	28.9
¹³ C ₂ -8:2 FTOH	448	415	10.8	3.4	11.2	6.7	22.5

5.3.6 Quality Assurance and Control (QA/QC)

The concentrations of target compounds were calculated using five points standard curve analysis for PFCAs (0.1-10 pg/μL), and FTOHs (10-1,000 pg/μL), in which the determination coefficients (R^2) were more than 0.99. Instrument detection limit (*IDL*) and instrument quantification limit (*IQL*) were defined as concentrations with signal to noise ratio (*S/N*) equal to 3:1 and 10:1, respectively. Method detection limit (*MDL*) and method quantification limit (*MQL*) were calculated from the *IDL* and *IQL*, respectively, when 500 mL was analysed for water samples (Table 5.3).

The recoveries in rainwater and river water samples were calculated from the absolute recoveries of mass-labeled standards (*i.e.* ¹³C₂-PFHxA, ¹³C₄-PFOA and ¹³C₂-PFDA). Amount of these standards recovered from the samples were calculated versus pure mass-labeled standard (unextracted). **Table 5.4** shows recoveries of mass-labeled standard PFCAs in the samples. For rainwater samples, the average recovery of ¹³C₂-

PFHxA, $^{13}\text{C}_4\text{-PFOA}$ and $^{13}\text{C}_2\text{-PFDA}$ ranged 69-84% for liquid-phase and 88-91% for solid-phase. The average recovery for river water samples in liquid- and solid-phase ranged 61-91% and 34-84%, respectively. All target compounds were not detected in the blank samples of rainwater and river water analysis. No correction procedure was adapted from mass-labeled standard recoveries and blank effects for all samples.

Table 5.4 Recoveries of mass-labeled standard PFCAs in water samples

List	Liquid-phase			Solid-phase		
	$^{13}\text{C}_2\text{-PFHxA}$	$^{13}\text{C}_4\text{-PFOA}$	$^{13}\text{C}_2\text{-PFDA}$	$^{13}\text{C}_2\text{-PFHxA}$	$^{13}\text{C}_4\text{-PFOA}$	$^{13}\text{C}_2\text{-PFDA}$
Rainwater (<i>n</i>)	8	8	8	8	8	8
Range	45-91	70-93	62-96	82-93	89-100	79-98
Average \pm S.D.	69 \pm 17	84 \pm 8	79 \pm 14	88 \pm 4	91 \pm 4	90 \pm 7
River water (<i>n</i>)	4	4	4	4	4	4
Range	87-96	73-77	57-67	29-38	70-86	80-90
Average \pm S.D.	91 \pm 5	75 \pm 2	61 \pm 5	34 \pm 4	75 \pm 8	84 \pm 5

5.3.7 Flux Calculation

Fluxes of target compounds *via* wet deposition were calculated using equation 5.1 (Kwok *et al.*, 2010; Taniyasu *et al.*, 2013a).

$$X = C \cdot V/A = C \cdot P \quad \text{eq. 5.1}$$

where X is the flux (ng/m^2) of a target compound in a rainfall event, C is the concentration of the compound in a rainwater sample (ng/L), V is the rainwater volume (L), A is the surface area of the sampler, and P is the precipitation amount (mm). The concentrations below *MDL* were assigned to be zero for flux calculation.

5.4 Results and Discussion

5.4.1 Concentration Levels of PFCAs and FTOHs in Rainwater Samples

All PFCAs were detected in rainwater samples, and total concentrations in both liquid- and solid-phase ranged from 7.3-28.7 ng/L (average = 15.1 ng/L) (**Fig. 5.3a**). PFCAs concentrations in each rainwater sample are detailed in **Appendix J**. PFHxA was detected in the highest concentrations (3.3-10.1 ng/L) in all samples. PFCAs in rainwater were dominant in liquid-phase (6.0-20.5 ng/L) which were 71-92% of their total concentrations in both phases (**Fig. 5.3b**). However, long chain PFCAs (C10-C12) were dominant in solid-phase and the proportion of PFCAs in solid-phase increased with increasing of fluorocarbon chain length, except for PFPeA (**Fig. 5.4**). In previous studies (Ahrens *et al.*, 2009; Ahrens *et al.*, 2010), sorption of PFCAs onto marine sediment was reported to increase with increasing fluorocarbon chain length, which was also found in this study. In addition, sediment organic carbon was the dominant parameter affecting the sorption, which increased with increasing organic carbon contents, indicating the importance of hydrophobic interactions (Higgins and Luthy, 2006). Therefore, organic carbon contents for particles in the air and rainwater should be further investigated.

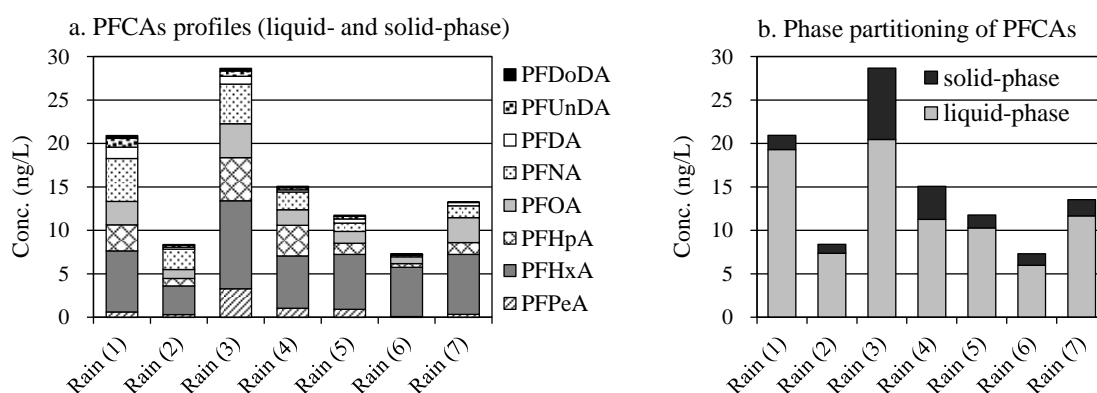


Figure 5.3 PFCAs profiles and their phase partitioning in rainwater samples

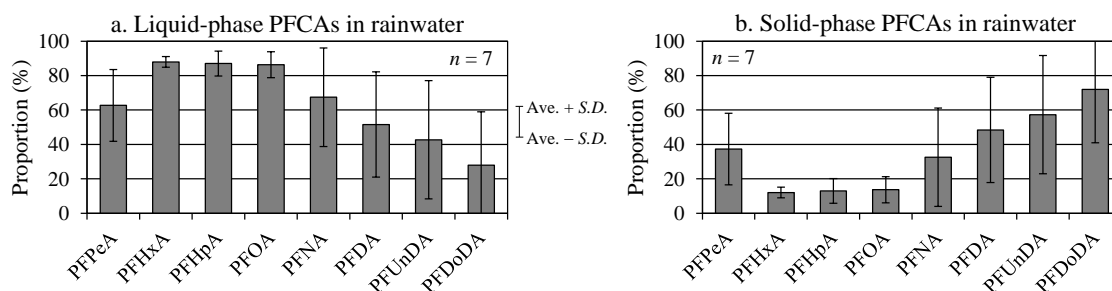


Figure 5.4 Proportion of liquid- and solid-phase of PFCAs in rainwater samples

Comparison of each PFCA and FTOH in air and rainwater samples in the same sampling location (Kyoto University) is shown in **Fig. 5.5**. All target compounds of PFCAs (90-190 pg/m³) were also detected in every air sample. This result indicated wet deposition of PFCAs from the air in the study area.

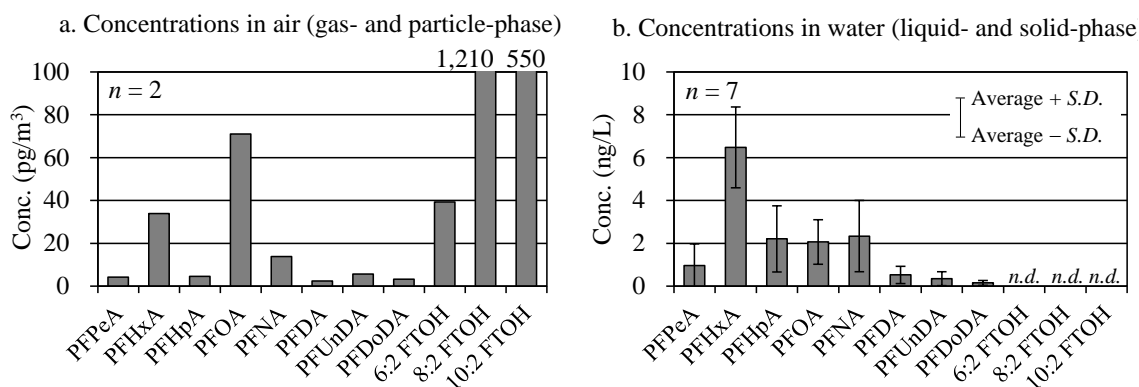


Figure 5.5 Concentrations of PFCAs and FTOHs in air and rainwater samples

All FTOHs (770-2,820 pg/m³) were detected in air and they were dominant in gas-phase, which only 8:2 FTOH was detected in the particle-phase (70 pg/m³). However, FTOHs in rainwater samples were below detection limits (<6.9 ng/L, <7.8 ng/L, and <8.7 ng/L for 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, respectively). FTOHs have relatively high vapor pressure, and low water solubility, compared to PFCAs. These properties indicate that FTOHs may be found mostly in gas-phase (Gauthier and Mabury, 2005), and difficult to be wet deposited from the air (Loewen *et al.*, 2005). Very few previous studies have reported FTOHs in aqueous environmental samples. The first study for rainwater was conducted in Kyoto, Japan by Mahmoud *et al.* (2009) and FTOHs were detected at very low concentrations (1.01-3.18 ng/L for 8:2 FTOH and <0.2-1.28 ng/L for 10:2 FTOH).

Therefore, rainwater samples in this study have the possibility to contain FTOHs to some extent, but at least they are not dominant compared with PFCAs. High sensitivity of the analytical method is needed for future studies.

5.4.2 Comparison of PFCAs in Rainwater with other Studies

PFCAs were detected in rainwater of several countries *i.e.* USA (Kim and Kannan, 2007; Kwok *et al.*, 2010), Germany (Dreyer *et al.*, 2010), France (Kwok *et al.*, 2010), China (Liu *et al.*, 2009; Kwok *et al.*, 2010), India and Japan (Kwok *et al.*, 2010). Average concentrations of total PFCAs (C5-C12) ranged between 1.1-51.1 ng/L (**Fig. 5.6**). The concentration in this study (Kyoto, Japan) was higher than those in most of the past researches, but it was not far different. PFCAs concentrations and profiles in rainwater can be influenced by many factors such as their presence and half-life in the atmosphere, physicochemical properties *i.e.* solubility and sorption onto particle, amount of rainfall and also meteorological conditions (Barton *et al.*, 2007; Rayne and Forest, 2009; Dreyer *et al.*, 2010; Taniyasu *et al.*, 2013a).

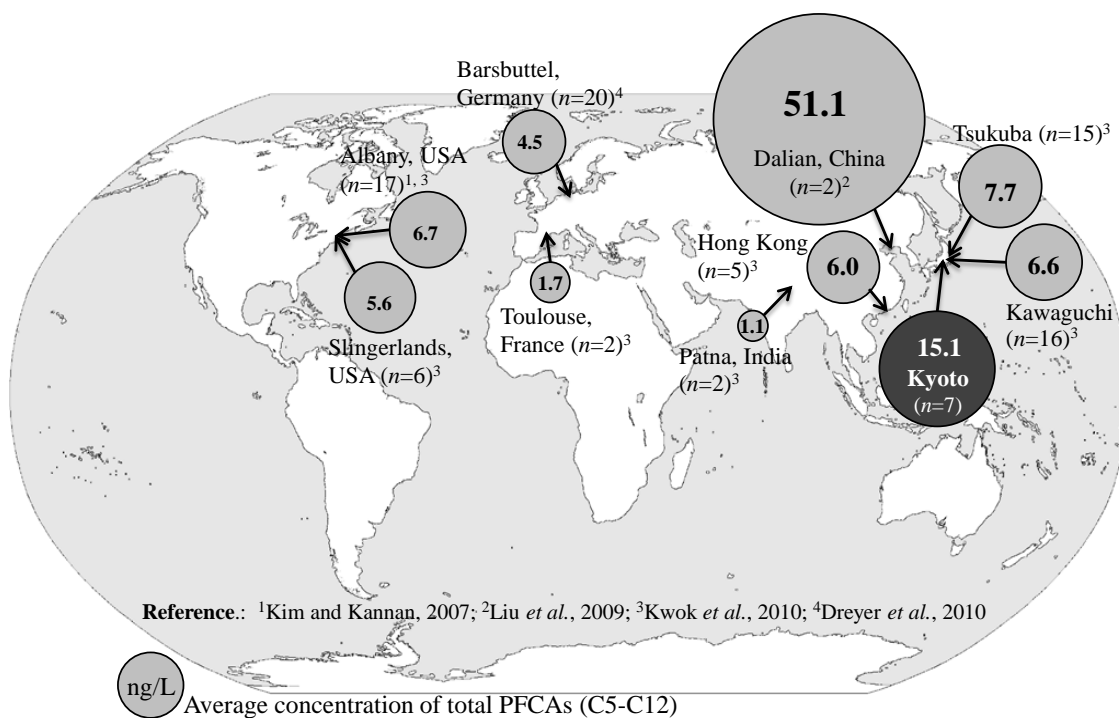


Figure 5.6 Comparison of PFCAs concentrations in this study (Kyoto, Japan) with other studies

5.4.3 Fluxes of PFCAs via Wet Deposition

Figure 5.7 shows fluxes of PFCAs for seven rainfall events. Total flux of eight PFCAs ranged between 120-1,830 ng/m² (average = 550 ng/m²). The highest flux was found in Rain (6), which had the highest amount of precipitation (250.5 mm). However, the highest concentration was found in Rain (3) and Rain (1), respectively. Antecedent dry weather period and cumulative sunshine duration before rainfall events are shown in Table 5.1 and scatter plot between these parameters and PFCAs concentrations are shown in **Fig. 5.8**. High correlations ($R>0.9$) were found between them, which indicated that long period of dry weather and high cumulative sunshine duration before rain increases the concentrations of PFCAs in the rainwater.

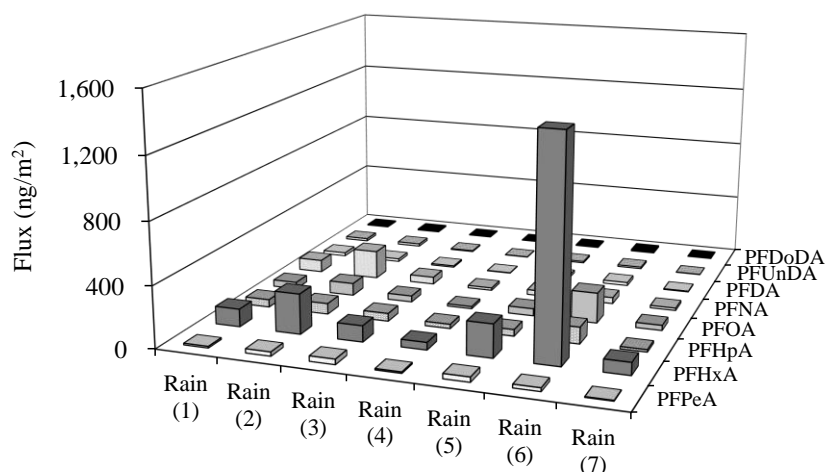


Figure 5.7 Fluxes of PFCAs *via* wet deposition

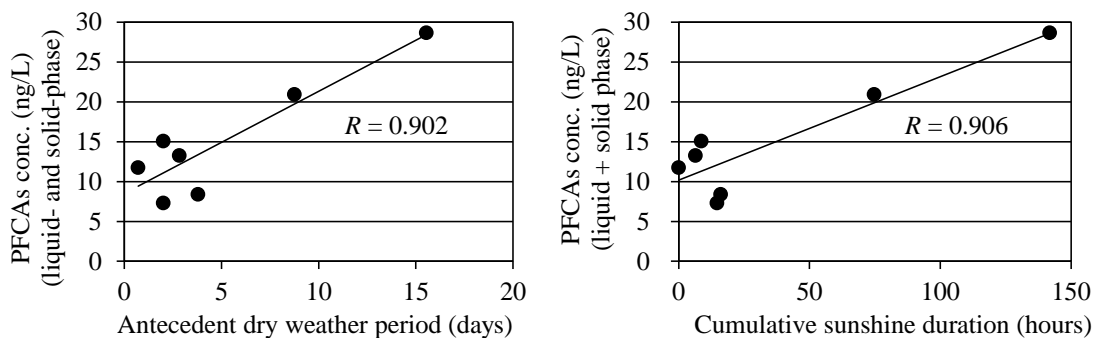


Figure 5.8 Scatter plots between PFCAs concentrations in rainwater samples and antecedent dry weather period and cumulative sunshine duration

Total annual precipitation in Kyoto, Japan in 2013 was 1,450.5 mm (Japan Meteorological Agency, 2013) and the estimated annual flux of eight PFCAs was 21,900 ng/m². The annual flux in this study was higher than those (**Fig. 5.9**) in Kawaguchi, Japan (10,050 ng/m²); Tsukuba, Japan (6,400 ng/m²); Slingerlands, USA (6,540 ng/m²) and Albany, USA (8,000 ng/m²), which were reported by Kwok *et al.* (2010).

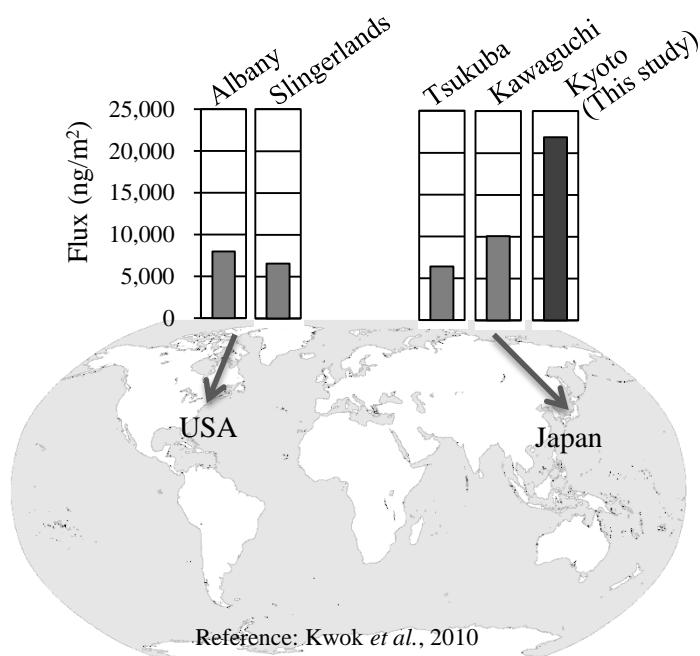


Figure 5.9 Comparison of total flux of PFCAs in this study with other studies

5.4.4 Photodegradation by Natural Sunlight

5.4.4.1 Rainwater Samples

During the sunlight exposure experiment of rainwater samples, temperatures of the samples ranged between 14.5–47.0°C, and the temperature of the surrounding air at the roof top ranged from 17.0°C to 42.5°C. UV intensity and illuminance of sunlight were between 0–108 mJ/cm² and 148–152,900 lux, respectively. Details of water and air temperatures, UV intensity and illuminance are shown in **Appendix K**. **Figure 5.10** shows the hourly average temperatures of the surrounding air and rainwater, and **Fig. 5.11** shows the hourly average UV intensity and illuminance. The highest temperature of

air and rainwater was observed at 1 pm, which coincided with the period of time for the highest illuminance and UV intensity.

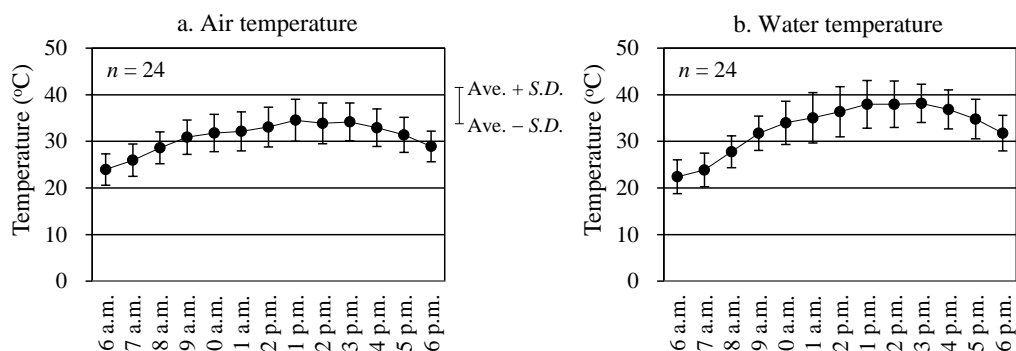


Figure 5.10 Hourly average temperatures of surrounding air and rainwater samples during a sunlight exposure experiment for rainwater samples

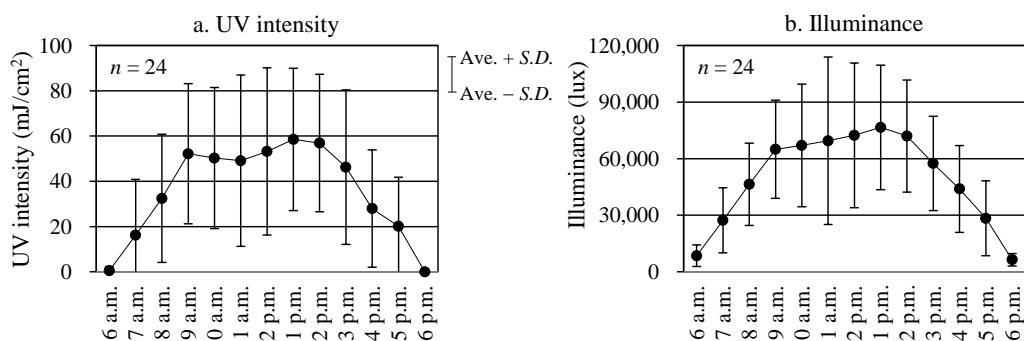


Figure 5.11 Hourly average UV intensity and illuminance during a sunlight exposure experiment for rainwater samples

Total UV intensity for exposure rainwater to sunlight was calculated based on the highest hourly UV intensity (measured in this study) and sunshine (Japan Meteorological Agency, 2013). Cumulative UV intensity for Rain (1) were 2,860 and 9,880 mJ/cm² for 1 week (June 1-7, 2013) and 4 weeks (June 1-28, 2013) of sunlight exposure, respectively (**Fig. 5.12a**). For Rain (2), UV intensity were 1,440 and 3,490 mJ/cm² for 1 week (June 22-28, 2013) and 2 weeks (June 22 to July 5, 2013) of sunlight exposure, respectively (**Fig. 5.12b**).

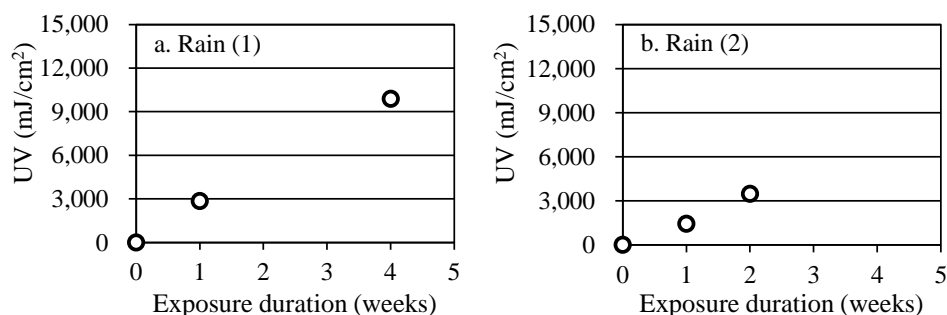


Figure 5.12 Cumulative UV intensity exposed to rainwater samples during a sunlight exposure experiment for rainwater samples

Figure 5.13 shows PFCAs concentrations during sunlight exposure of Rain (1). After four weeks of sunlight exposure, most of PFCAs in Rain (1) reached their maximum concentrations. The concentrations of PFCAs increased in the range from 0.14 ng/L (PFDoDA) to 3.96 ng/L (PFHxA). The rates of increase were 32% for PFPeA, 56% for PFHxA, 96% for PFHpA, 72% for PFOA, 46% for PFNA, 176% for PFDA, 100% for PFUnDA and 45% for PFDoDA. These findings suggested that precursor compounds of PFCAs were also wet deposited from the atmosphere and later degraded in water environment by natural sunlight. Although FTOHs were measured in all of the samples, none of FTOHs was detected.

Figure 5.14 shows PFCAs concentrations during sunlight exposure of Rain (2). Most of PFCAs in Rain (2) reached their maximum concentrations after two weeks of sunlight exposure. The concentrations of PFCAs increased from 0.06 ng/L (PFPeA) to 3.86 ng/L (PFNA). The rates of increase in Rain (2) were 18% for PFPeA, 42% for PFHxA, 33% for PFHpA, 47% for PFOA, 164% for PFNA, 186% for PFDA, 72% for PFUnDA and 158% for PFDoDA. Similar results, that is, increasing PFCAs concentration, were observed in Rain (1) and Rain (2) which indicated wet deposition and degradation of their precursor compounds. PFCAs in Rain (1) and Rain (2) increased mainly in liquid-phase, which may suggest the importance of photodegradation reactions in liquid-phase.

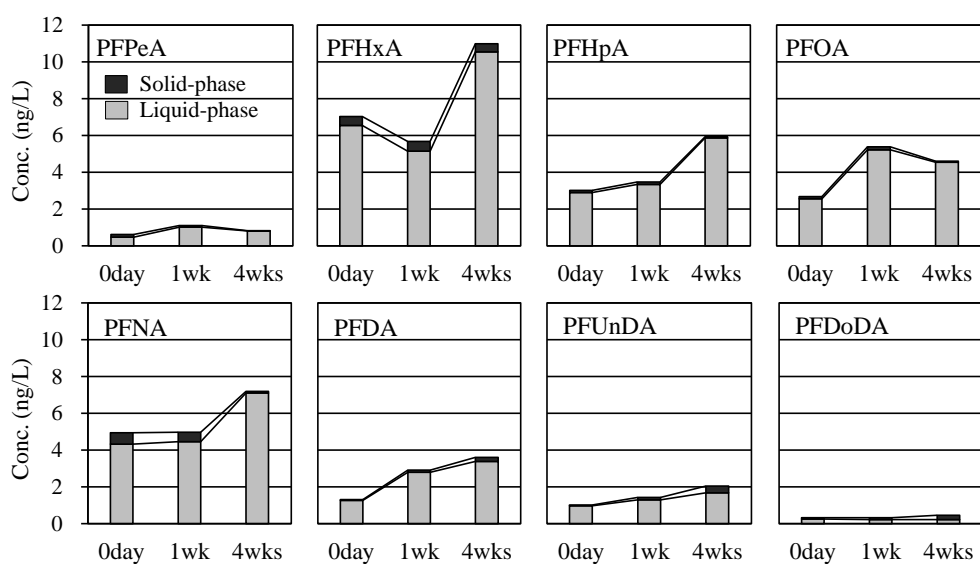


Figure 5.13 Changes in PFCAs concentrations in Rain (1) after 1 week and 4 weeks of sunlight exposure during June 1-28, 2013

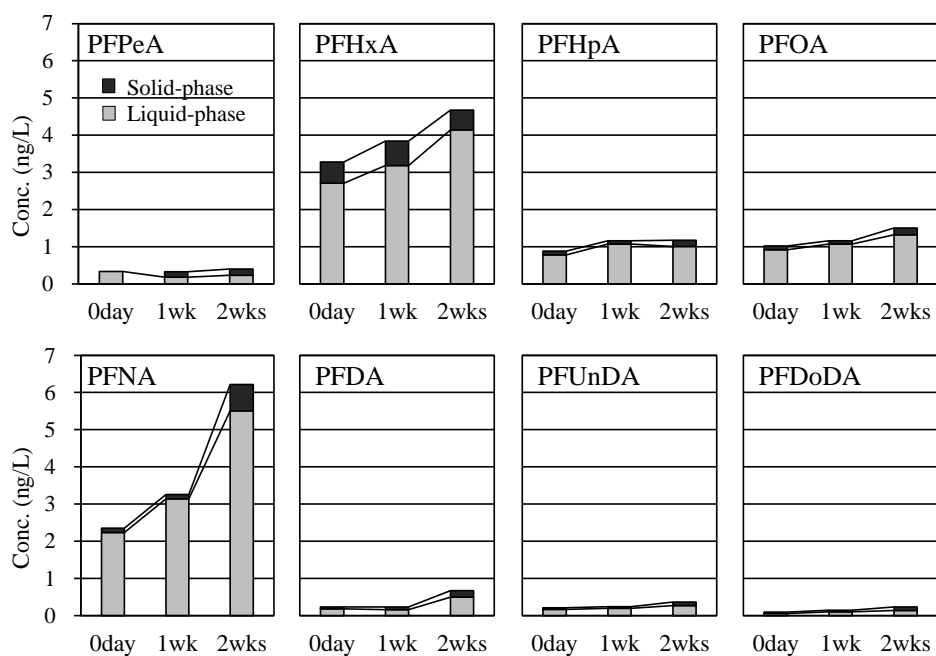


Figure 5.14 Changes in PFCAs concentrations in Rain (2) after 1 week and 2 weeks of sunlight exposure during June 22 to July 5, 2013

5.4.4.2 Solution of 8:2 FTOH in *Ultrapure* Water Samples

The sunlight exposure experiment of 8:2 FTOH solutions was conducted in Japan during July 16 to October 17, 2013. 8:2 FTOH decreased after sunlight exposure (**Fig. 5.15**) and the remaining 8:2 FTOH was 60% for 12 weeks of sunlight exposure. This result indicated 8:2 FTOH was photo-degraded by sunlight. Taniyasu *et al.* (2013) also reported that FTOHs were photo-degraded by natural sunlight in the high mountain area. The degradation rate of 6:2 FTOH and 8:2 FTOH after 1,232 hours of sunlight exposure was 75% and 90%, respectively. The remaining 8:2 FTOH in control sample was 94%. Therefore, degradation of 8:2 FTOH except photodegradation was neglected. PFPeA, PFHxA and PFNA were detected in the samples exposed sunlight (Fig. 5.15). The maximum rate was only 0.2% (PFHxA) of initial concentration 8:2 FTOH (1,000 ng/L), which showed a small portion compared to degradation rate of 8:2 FTOH (40%). This result suggested that FTOHs were not immediately and directly formed to PFCAs. Details of 8:2 FTOH and PFCAs concentrations in the samples are shown in **Appendix J**.

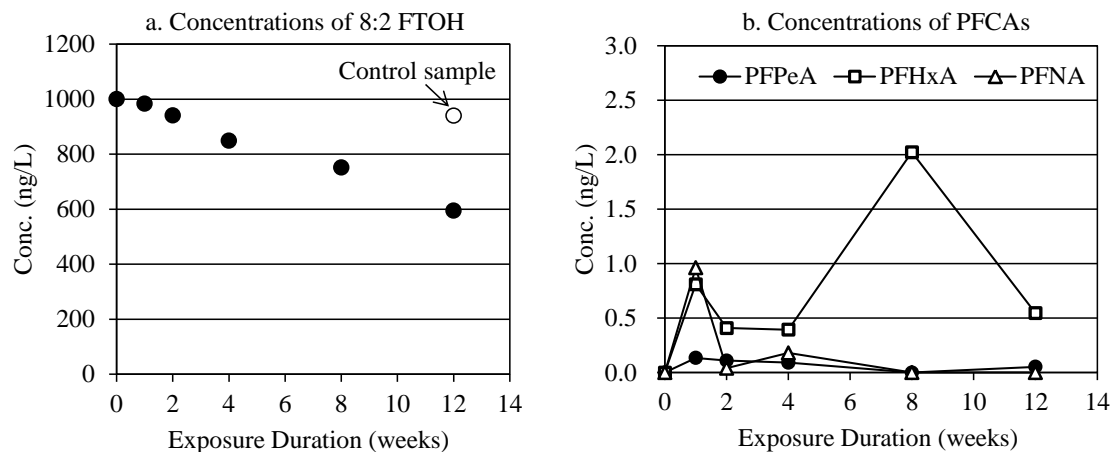


Figure 5.15 Concentrations of 8:2 FTOH and PFCAs in spiked *ultrapure* water samples during sunlight exposure

5.4.4.3 River Water Samples

Total concentration of PFCAs (C5-C12) in Chao Praya River at the sampling day (Day0) was 2.70 ng/L. Four PFCAs (C5-C8) were detected in liquid-phase, and two

PFCAs (C8 and C10) were detected in solid-phase (**Fig. 5.16**). PFPeA and PFOA were dominant compounds in PFCAs.

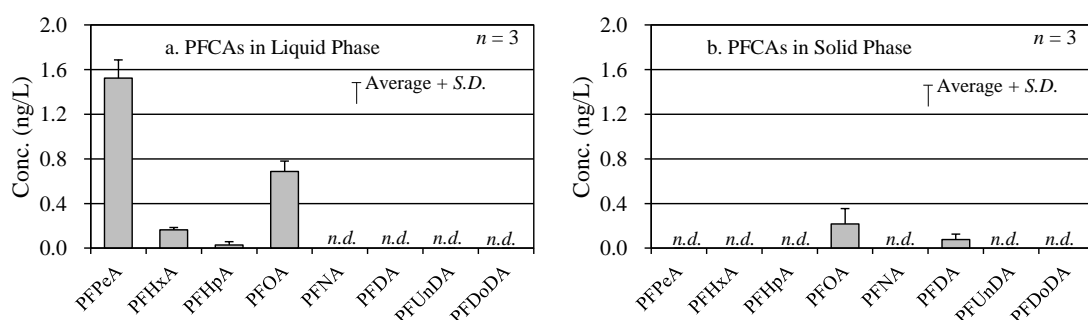


Figure 5.16 PFCAs concentrations in liquid- and solid-phase of river water samples at the sampling day (Day0)

During the sunlight exposure experiment of river water samples, temperatures of the samples ranged between 19.6-32.0°C and the temperature of surrounded air at the roof top ranged 19.5-36.8°C. UV intensity and illuminance of sunlight were between 0-113 mJ/cm² and 2-83,730 lux, respectively. Appendix K also shows measurement of these sunlight parameters in Thailand. **Figure 5.17** shows hourly average temperatures of surrounded air and river water, and **Fig. 5.18** shows hourly average UV intensity and illuminance. Temperatures of air and water rapidly increased from 9 a.m. until 2 p.m. and slowly decreased until 6 p.m. High UV intensity and illuminance were observed during 10 a.m. to 2 p.m. during daytimes. Compared to Japan, average UV intensity and illuminance were observed slightly higher in Thailand.

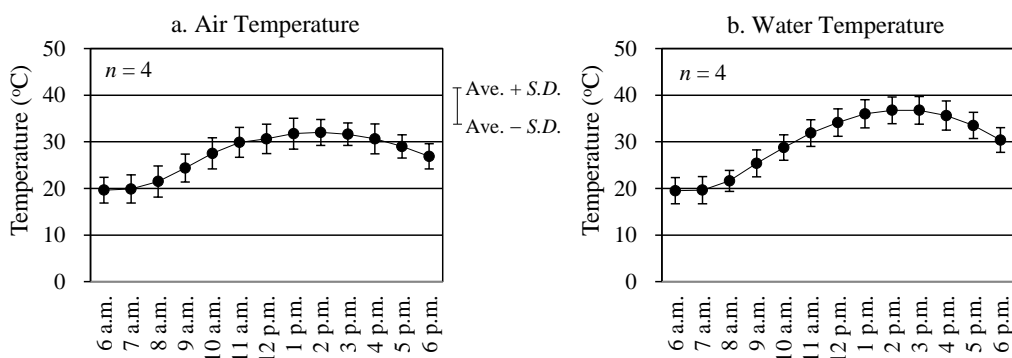


Figure 5.17 Hourly average temperatures of surrounded air and river water sample during a sunlight exposure experiment for river water samples

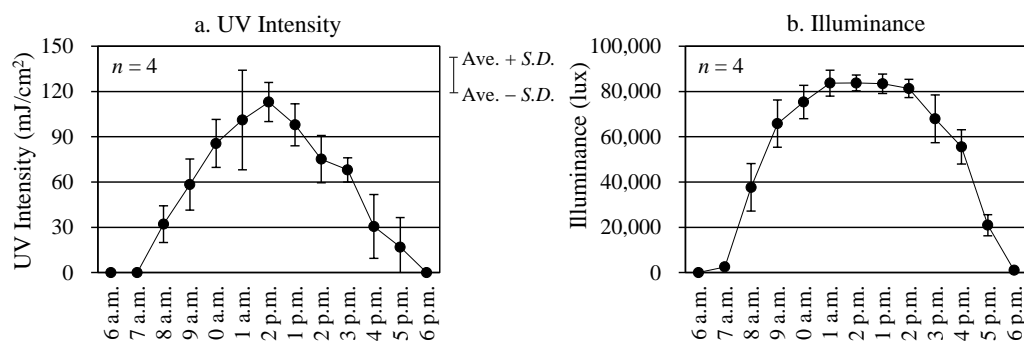


Figure 5.18 Hourly average UV intensity and illuminance during a sunlight exposure experiment for river water samples

Figure 5.19 shows concentrations of PFCAs in river water samples (no spike of 8:2 FTOH) during sunlight exposure and **Fig. 5.20** shows the concentrations for the spiked samples (spike 1,000 ng/L of 8:2 FTOH into river water samples). Most of PFCAs in river water samples increased their concentrations after four weeks of sunlight exposure. For the no spiked samples, the rates of increase of PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA and PFUnDA were 190%, 33%, 40%, 373%, 56%, 83% and 9%, respectively. For the spiked samples, the rates of increase of PFPeA, PFHxA, PFHpA, PFOA, PFNA and PFDA were 372%, 48%, 150%, 596%, 13% and 13%, respectively. Most of the increase rates of PFCAs in the spiked samples were slightly higher than those in the no spiked samples.

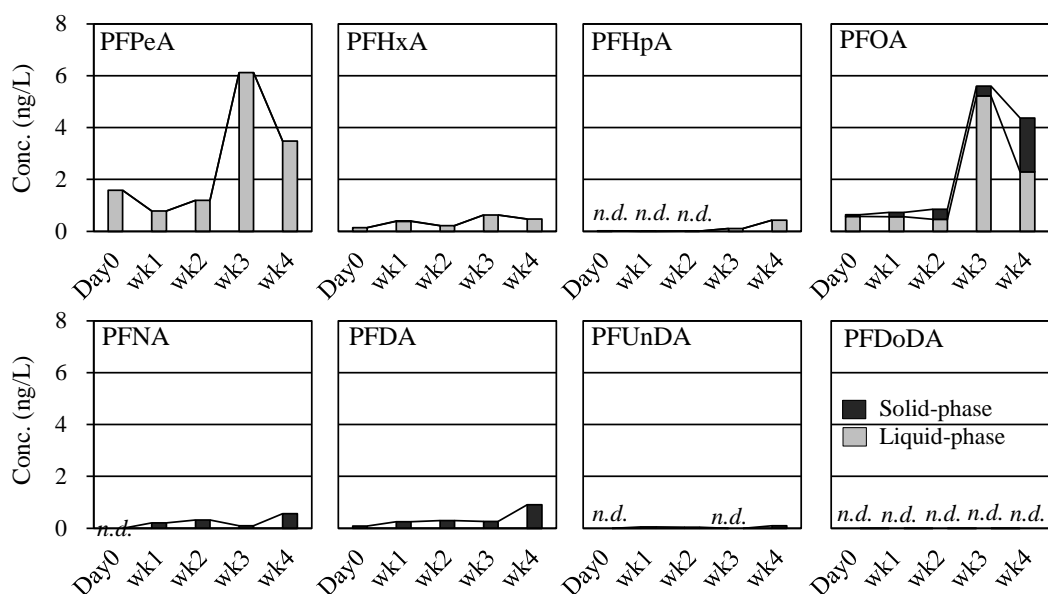


Figure 5.19 Changes in PFCAs concentrations in river water samples (no spike of 8:2 FTOH) during a sunlight exposure experiment

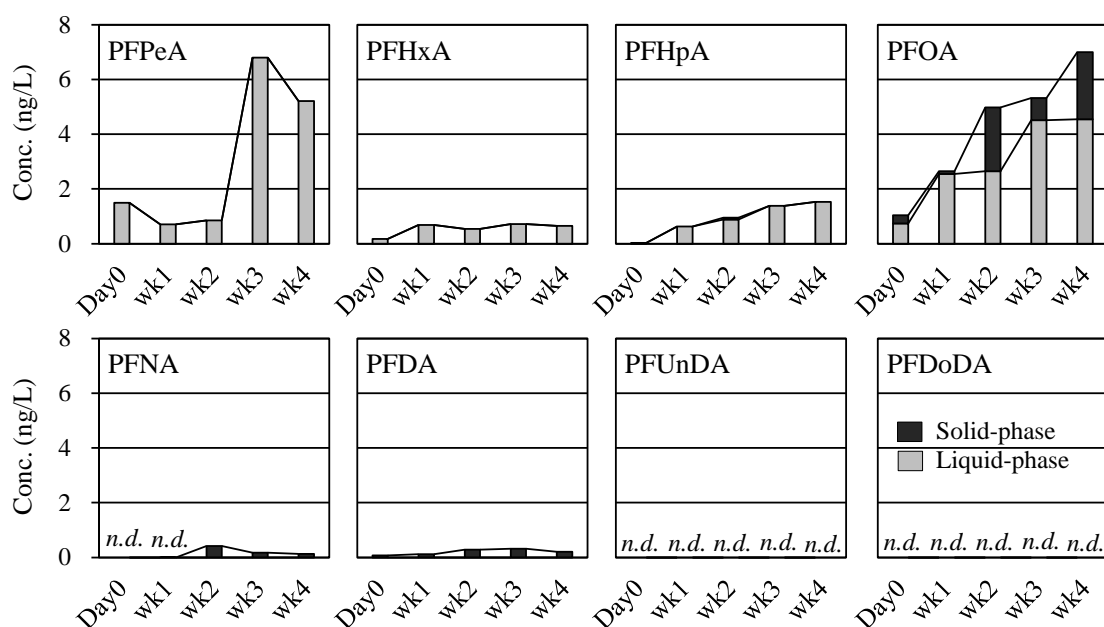


Figure 5.20 Changes in PFCAs concentrations in river water samples (spike 1,000 ng/L of 8:2 FTOH) during a sunlight exposure experiment

5.4.5 Distribution Pathways of PFCAs and FTOHs

This study investigated PFCAs and FTOHs in air and rainwater samples. PFCAs were detected in every air and rainwater sample, which indicated their distribution pathways from air to water environment *via* wet deposition (**Fig. 5.21**). PFCAs in rainwater samples obviously increased after a few weeks of sunlight exposure, which indicated degradation of their precursor compounds. FTOHs were detected in relatively high concentrations in the air, compared to PFCAs, but their occurrences in rainwater samples were below the detection limits. This result showed that wet deposition may be less effective for atmospheric removal of FTOHs. Therefore, increase of PFCAs in rainwater samples after sunlight exposure might have been contributed by FTOH's intermediates or other precursor compounds for which wet deposition was effective. Further investigation by on-site and laboratory experiments is needed to confirm the contribution of PFCAs from these intermediates and other precursor compounds.

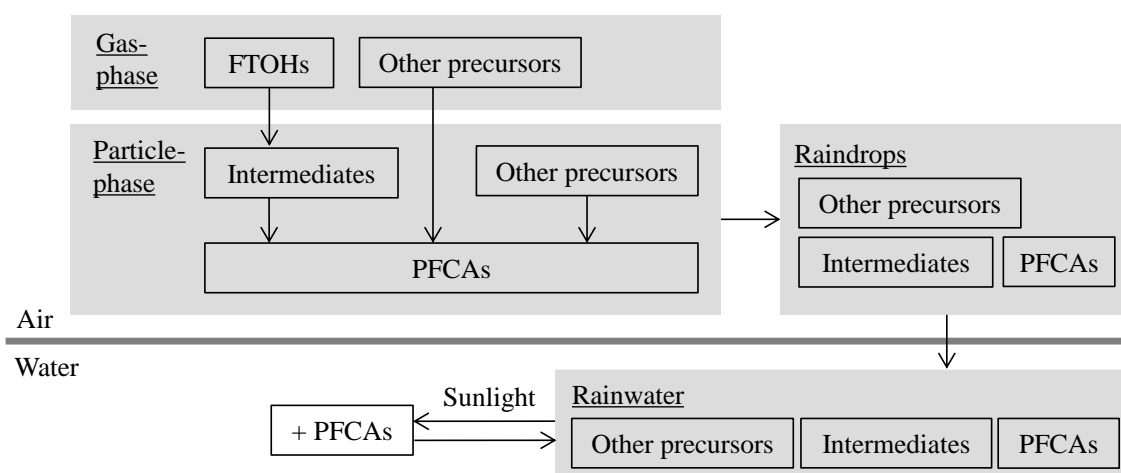


Fig. 5.21 Suggested distribution pathways of PFCAs and FTOHs from air to water environment

5.4 Summary

All PFCAs were detected in rainwater samples and PFHxA was the dominant compounds. Total concentrations of PFCAs ranged from 7.3-28.7 ng/L and they were dominant in liquid-phase (71-92%). However, solid-phase partitioning increased with increasing of fluorocarbon chain length. PFCAs concentration in rainwater in this study (Kyoto, Japan) was higher than those in most of past researches but it was not far different. All PFCAs (90-190 pg/m³) were also detected in air at the same sampling location. This result indicated distribution of PFCAs from air to water *via* wet deposition.

Total amount of precipitation during sampling period was 8.1-250.5 mm and total flux of PFCAs ranged between 120-1,830 ng/m². Total annual precipitation in Kyoto in 2013 was 1,450.5 mm and estimated annual flux of PFCAs was 21,900 ng/m². High precipitation amount showed high flux of PFCAs. Long period of dry weather and high cumulative sunshine hours before rain increases the concentrations of PFCAs in rainwater.

All FTOHs were detected at very high concentrations (770-2,820 pg/m³) in air samples, but the concentrations in rainwater samples were below the detection limits (<6.9-8.7 ng/L). Therefore, wet deposition might be less effective for atmospheric removal of

FTOHs. Most of PFCAs in rainwater samples increased (18-186%) after a few weeks of sunlight exposure, which indicated degradation of their precursor compounds by sunlight. However, a small portion of PFCAs (0.2%) was formed after exposure of 8:2 FTOH solutions to sunlight, whereas 40% of 8:2 FTOH was degraded. Therefore, the increases of PFCAs in rainwater samples might have been contributed by FTOH's intermediates or other precursor compounds for which wet deposition was effective.

Five PFCAs (C5-C8, C10) were detected in river water (Chao Praya River) with total concentration of 2.70 ng/L. Most of PFCAs in river water samples increased their concentrations after sunlight exposure. Increasing rates of PFCAs in spiked samples (1,000 ng/L of 8:2 FTOH) ranged 13%-596%, which were slightly higher than those in the no spiked samples (9%-373%). This result also indicated photodegradation of PFCA's precursor compounds in water environment by natural sunlight.

Chapter 6

Photodegradation Rates of 8:2 FTOH and Formation of it By-products

6.1 Introduction

Fluorotelomer alcohols (FTOHs) are degradable in natural conditions and they were suggested as precursor compounds of perfluoroalkyl carboxylates (PFCAs) in environment. While FTOHs were widely detected in the environment but their contribution to PFCAs is unclear.

FTOHs were widely detected in ambient and indoor air of many countries including the Arctic's and Atlantic's atmosphere so that they may play an important role as the potential sources of PFCAs in environment. Laboratory and field studies have shown degradation of FTOHs in several environmental media such as soil, activated sludge, water and air via bio-degradation (Dinglasan *et al.*, 2004; Wang *et al.*, 2005; Liu *et al.*, 2007; Wang *et al.*, 2009), photodegradation (Gauthier and Mabury 2005; Taniyasu *et al.*, 2013) and atmospheric oxidation (Ellis *et al.*, 2004; Styler *et al.*, 2013), and in vivo and vitro experiments via metabolisms (Kudo *et al.*, 2005; Martin *et al.*, 2005; Fasano *et al.*, 2006; Henderson *et al.*, 2007; Nabb *et al.*, 2007). Degradability of FTOHs was confirmed and PFCAs were observed as their degradation products in mentioned previous studies. However, degradation mechanisms of FTOHs, especially for other unidentified pathways and intermediates, have not been well established.

This study imitates long-time photodegradation of FTOHs in natural sunlight with a short duration by conducting a laboratory experiment using UV irradiation. Degradation rates of FTOHs and formation of PFCAs and other by-products were investigated. These results could provide degradation mechanism of FTOHs and their contribution to PFCAs in environment.

6.2 Objectives

The purposes of this chapter were (1) to examine photodegradation rate of 8:2 FTOH using UV (254 nm) irradiation, (2) to quantify PFCAs by SIM mode of HPLC-MS/MS and calculate their formation rates, and (3) to identify other degradation by-products of 8:2 FTOH by SCAN mode HPLC-MS/MS.

6.3 Methodology

6.3.1 Chemicals and Standards

Nine target compounds of 8:2 FTOH, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA and PFDODA were purchased from Wako Pure Chemicals (Osaka, Japan). Analytical or HPLC grade were used for all solvents and reagents. *Ultrapure* water was prepared by passing *Milli-Q* water through PrecepC-Agri (C18) cartridges (Wako, Japan) inline connected to Oasis[®]HLB cartridges (Waters, Japan) to remove any PFCAs from *Milli-Q* water.

6.3.2 UV Irradiation Procedures

A UV irradiation experiment was conducted with a UV reactor (**Fig. 6.1**) at a laboratory in Kyoto University. The reactor was comprised of a stainless steel cylinder (L-500 UA, ϕ 64 mm x 580 mm, Nippo Electric Co., Ltd., Kanagawa, Japan), a quartz glass vessel and a UV lamp (SGL-1000T4U/L, 254 nm, 35 watts, 12 mW/cm², Nippo Electric Co., Ltd., Kanagawa, Japan). The vessel was placed at the center of the cylinder, and the UV lamp was inserted in the vessel for irradiation. An aqueous solution of 8:2 FTOH with three initial concentrations *i.e.* 1,000 ng/L (2.16 nmol/L), 10,000 ng/L (21.6 nmol/L), and 100,000 ng/L (216 nmol/L) was prepared in *ultrapure* water. The solution (800 mL) was poured into the UV reactor as a batch condition for irradiation time of 1, 2, 4, 8 and 24 hours. A control test was prepared similar to the irradiated samples but without UV irradiation.

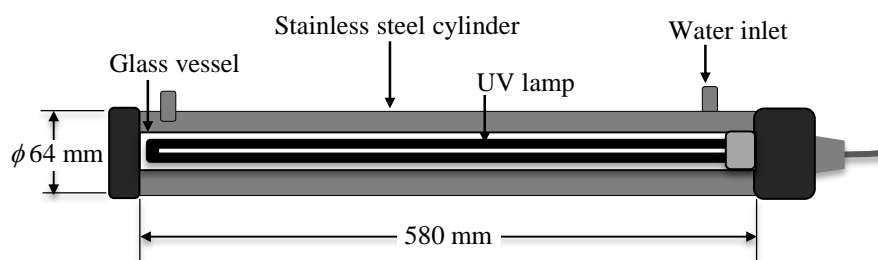


Figure 6.1 UV reactor

6.3.3 Analytical Procedures for 8:2 FTOH

For extraction procedure of 8:2 FTOH, 15 mL of methyl tetra butyl ether (MTBE) was added to an irradiated sample (100 mL) in a separation funnel and the sample were thoroughly shaken for 3 minutes. The dissolved 8:2 FTOH in MTBE layer was collected into a polypropylene (PP) centrifuge tube after discarding the bottom layer of water. This extraction was repeated 3 times (about 45 mL of extracts in total). After that, the solvent was dried chemically by Na_2SO_4 , solvent exchanged to methanol and reduced to 1 mL using nitrogen gas. Analytical procedures for 8:2 FTOH are shown in **Fig. 6.2**

8:2 FTOH was quantified by Agilent 6890 gas chromatography (GC)/ Agilent 5973 mass spectrometer (MS) in electron ionization mode using selective ion monitoring. Analytical parameters of 8:2 FTOH *i.e.* quantifier and qualifier ions and retention time (*RT*) are shown in **Table 6.1**. The purified extracts (2 μL) were injected to GC-MS with splitless mode at a temperature of 230°C. The target compounds were separated on 30 m DB-WAX capillary column with 0.25 mm inner diameter and 0.25 μm film thickness. Helium was used as a carrier gas at a constant flow of 1 mL/min. The GC oven was set at 50°C for 5 min, increased to 240°C with a ratio of 10°C/min (19 min) and held at 240°C for 1 min, resulting in total run time of 25 min. Ion source and quadrupole temperatures were 230°C and 150°C, respectively.

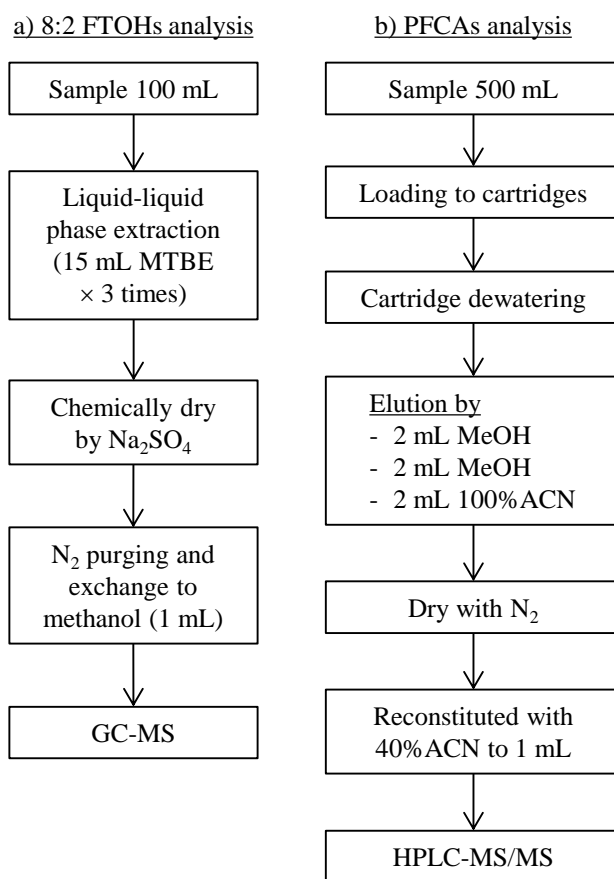


Figure 6.2 Analytical procedures of 8:2 FTOH and PFCAs in water samples

Table 6.1 Analytical parameters for 8:2 FTOH and PFCAs

Compounds	Ion 1 (<i>m/z</i>)	Ion 2 (<i>m/z</i>)	<i>RT</i> (min)	<i>IDLs</i> (ng/mL)	<i>IQLs</i> (ng/mL)	<i>MDLs</i> (ng/L)	<i>SQLs</i> (ng/L)
<u>GC-MS</u>	<u>Quantifier ion</u>	<u>Qualifier ion</u>					
8:2 FTOH	444	463	10.9	3.9	13.1	7.8	26.1
<u>HPLC-MS/MS</u>	<u>Parent ion</u>	<u>Daughter ion</u>					
PFPeA	263	219	1.8	0.01	0.04	0.03	0.09
PFHxA	313	269	2.6	0.01	0.03	0.02	0.05
PFHpA	363	319	4.6	0.01	0.03	0.02	0.06
PFOA	413	369	7.1	0.01	0.04	0.02	0.08
PFNA	463	419	9.9	0.02	0.07	0.04	0.15
PFDA	513	469	12.5	0.01	0.03	0.02	0.05
PFUnDA	563	519	15.1	0.01	0.04	0.02	0.07
PFDoDA	613	569	17.7	0.01	0.04	0.02	0.08

6.3.4 Analytical Procedures for Degradation By-products (PFCAs and others)

For analytical procedure degradation by-products, an irradiated sample (500 mL) was loaded to PrecepC-Agri (C18) cartridge inline connected to Oasis[®] HLB cartridge using a Sep-Pak concentrator at a flow rate of 5 mL/min. Both cartridges were manually pre-conditioned by 10 mL of methanol and 20 mL of *ultrapure* water. The concentrator was pre-washed by methanol for 5 min at 5 mL/min followed by *ultrapure* water for 15 min at 5 mL/min before using. After sample loading, the cartridges were dried by a vacuum manifold (Water, USA) for two hours. Target compounds in dried cartridges were eluted twice by 2 mL methanol, followed by 2 mL of acetonitrile. Then, the elute solution was evaporated until dried by nitrogen gas and reconstituted using HPLC-MS/MS mobile phase to 1 mL. Figure 6.1 also shows analytical procedures for PFCAs.

PFCAs were analysed by Agilent 1200SL high performance liquid chromatography (HPLC) coupled with Agilent 6400 Triple Quadrupole mass spectrometer (MS/MS) in electrospray ionization negative mode using multiple reactions monitoring. The purified extracts (10 µL) were injected to Agilent Eclipse XDB-C18 column (inner diameter 2.1 mm, length 100 mm and particle size 5 µm). The mobile phase consisted of (A) 5 mM ammonium acetate in *ultrapure* water and (B) 100% acetonitrile. At a flow rate of 0.25 mL/min, separation process started with initial condition of 30% (B), increased to 50% (B) at 16.5 min, then to 70% (B) at 16.6 min and hold at 70% (B) for 3.4 min, after that went up to 90% (B) at 21 min and kept at 90% (B) for 1 min, and then ramped down to 30% (B), resulting a run time of 34 min. PFCAs were quantified using selective ion monitoring (SIM) mode. Table 6.1 also shows analytical parameters of PFCAs *i.e.* parent and daughter ions and retention time (*RT*). For identifying other degradation by-products, the extracted samples were analysed by scanning (SCAN) mode of HPLC-MS/MS. A range of mass-to-charge (*m/z*) ratios from 10 to 500 were monitored.

6.3.5 Quality Assurance and Control (QA/QC)

For recovery determination, native standards of the target compounds (*i.e.* 8:2 FTOH, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA and PFDoDA) were spiked into *ultrapure* water, and subjected to the extraction procedure outlined for irradiated samples. Average recovery was 43% for 8:2 FTOH and ranged from 44% (PFDoDA) to 101% (PFHxA) for PFCAs (Table 6.2). A control test was conducted to check any contamination of PFCAs in the aqueous solution of 8:2 FTOH. Three sets of 8:2 FTOH solutions (1,000 ng/L, 10,000 ng/L and 100,000 ng/L) were prepared for the control samples (no UV irradiation). They were then extracted following the same procedure as for irradiated samples and analyzed for PFCAs using SIM mode of HPLC-MS/MS. All PFCAs were not detected in the control sample for initial concentration of 1,000 ng/L. For the initial concentrations of 10,000 and 100,000 ng/L, PFHxA, PFOA and PFNA were detected in the control samples (Table 6.3). Therefore, the experimental results were corrected by recoveries and the values in control samples.

Table 6.2 Method recovery of 8:2 FTOH and PFCAs

Items	Recovery (%)								
	8:2 FTOH	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
<i>n</i>	3	5	5	5	5	5	5	5	5
Average±S.D.	43±11	89±10	101±5	92±6	95±6	95±5	83±10	64±12	44±9
Range	35-55	79-104	96-110	87-102	91-105	92-102	75-101	57-85	38-59

Table 6.3 PFCAs in control samples (No UV irradiation)

Control samples	Concentration (ng/mL)							
	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
8:2 FTOH-1,000 ng/L	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
8:2 FTOH-10,000 ng/L	<i>n.d.</i>	0.76	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
8:2 FTOH-100,000 ng/L	<i>n.d.</i>	0.70	<i>n.d.</i>	5.71	0.28	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>

Due to potential absorption of PFCAs onto glass surface, absorption test samples (*n* = 2) were prepared by spiking mixed PFCAs (C5-C12) into *ultrapure* water and poured into UV reactor for 8 hours (without UV irradiation) to check their absorption onto glass surface of UV reactor. The samples were extracted following the same procedure as for irradiated samples and analyzed by SIM mode of HPLC-MS/MS. The results showed that long-

chain PFCAs tended to be absorbed at the reactor's surface, which were 8%, 21% and 28% for PFDA, PFUnDA and PFDoDA, respectively. According to this effect, the reactor was rinsed with methanol and the rinses were transferred to the elute solution, and were further evaporated by nitrogen gas for HPLC-MS/MS analysis. After finishing each irradiation batch, the UV reactor was cleaned by rinsing twice with methanol and 4 times with *ultrapure* water.

The concentrations were calculated using five points standard curve analysis for 8:2 FTOH (10-1,000 ng/mL), and PFCAs (0.1-10 ng/mL), in which coefficients of determination (R^2) were more than 0.99. Instrument detection limit (*IDL*) was defined as concentrations with signal to noise ratio (*S/N*) equal to 3:1. Instrument quantification limit (*IQL*) was used for quantifying analytes, and defined by *S/N* 10:1. Method detection limit (*MDL*) and method quantification limit (*MQL*) were calculated from the *IDL* and *IQL*, respectively, when 500 mL of sample was analyzed (Table 6.1).

6.4 Results and Discussion

6.4.1 Photodegradation Rates and Kinetics of 8:2 FTOH

Figure 6.3 shows UV intensity and water temperature during the UV irradiation experiment. UV intensity for 1, 2, 4, 8 and 24 hours of irradiation was 0.04, 0.09, 0.17, 0.35 and 1.04 kJ/cm², respectively. Reaction temperature during the experiments was increased from 20°C (water sample's temperature, no irradiation), 44.0°C (1 hour of irradiation), 54.5°C (2 hours), 61.0°C (4 hours), and then constant at 64.0°C after 8 hours.

8:2 FTOH was found to degrade at a very fast rate under a UV (254 nm) irradiation experiment (**Fig. 6.4**). 8:2 FTOH was not detected after 24 hours of UV irradiation for the initial concentration of 2.16 nmol/L and 21.6 nmol/L, and remained 3.52 nmol/L (1.63%) for the highest initial concentration (216 nmol/L). First-order kinetic was used to simulate the degradation of 8:2 FTOH as shown in **Fig. 6.5** and the corresponding rate constant was 0.228 hour⁻¹, 0.298 hour⁻¹ and 0.188 hour⁻¹ for the initial concentration of 2.16 nmol/L, 21.6 nmol/L and 216 nmol/L respectively. Half-life of 8:2 FTOH by

direct photolysis (UV 254 nm) in this study was between 2.3-3.7 hours. Gauthier and Mabury (2005) conducted indirect photolysis experiments (irradiated in a suntest photosimulator, 290-800 nm) of 8:2 FTOH using hydroxyl radicals (10 mM hydrogen peroxide solution) as a degradation agent, and its half-life was 0.83 hours. Half-life of 8:2 FTOH by aerobic biodegradation using a mix microbial system was estimated as 4.4 hours (Dinglasan *et al.*, 2004). Thus, degradation of 8:2 FTOH by photolysis was faster than that by bio-degradation, indicated photodegradation might be a major degradation pathway of 8:2 FTOH in water environment.

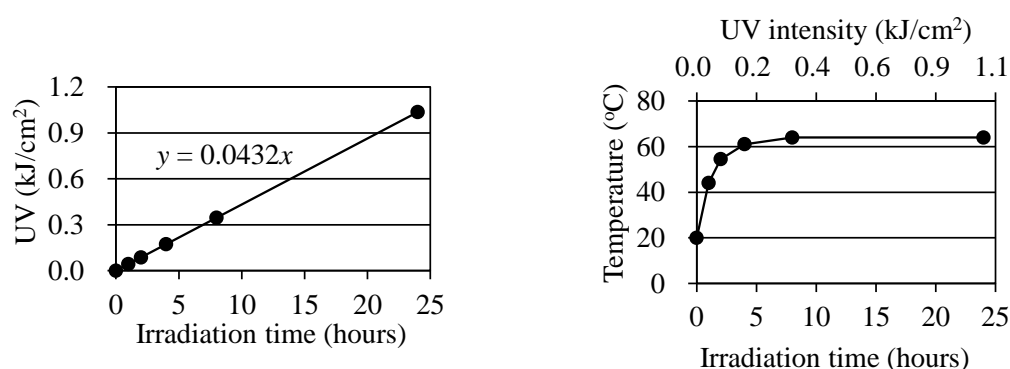


Figure 6.3 UV intensity with irradiation time and temperature of aqueous samples during UV irradiation

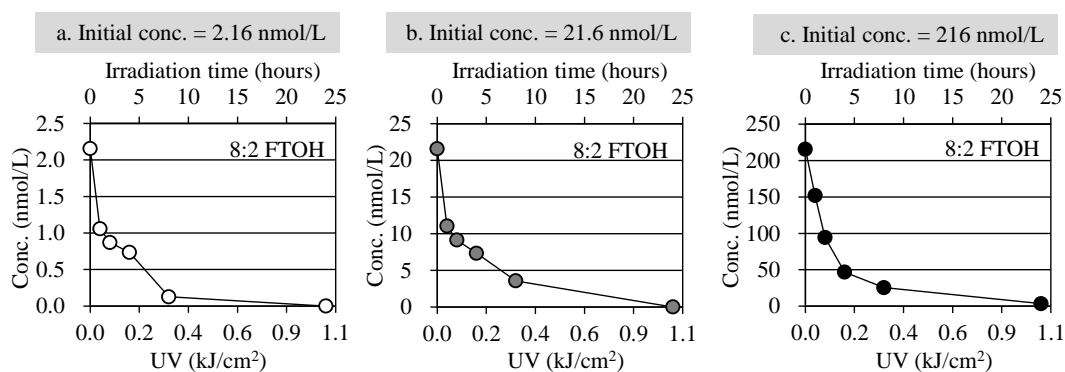


Figure 6.4 Reduction of 8:2 FTOH concentrations during UV irradiation

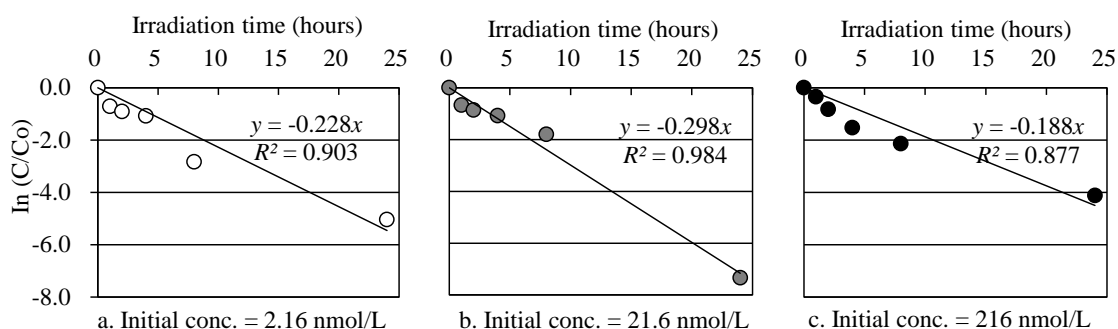


Figure 6.5 Kinetics of 8:2 FTOH degradation by UV light (254 nm)

6.4.2 Production Rates of PFCAs

Five PFCAs with carbon chain lengths of 5-9 (C5-C9) were formed as degradation by-products of 8:2 FTOH (**Fig. 6.6**) and these PFCAs increased while 8:2 FTOH decreased with irradiation time. For the lowest initial concentration of 8:2 FTOH *i.e.* 2.16 nmol/L, the highest of PFCAs concentration (0.04 nmol/L) were detected at 4 hours of UV irradiation with the production rate of 1.76% at molar basis. After 4 hours of irradiation, PFCAs decreased which suggested further degradation to form other per- or polyfluoroalkyl substances.

For higher initial concentrations of 8:2 FTOH *i.e.* 21.6 nmol/L and 216 nmol/L, only PFNA (C9) reached its maximum concentration after 4 hours and 8 hours of UV irradiation, respectively. Other PFCAs (C5-C8) increased their concentrations and reached the maximum concentration after 24 hours of irradiation. Degradation of long chain PFCAs by UV irradiation and formation of their short chain were also observed in previous studies (Chen *et al.*, 2007, Lee *et al.*, 2009). After 24 hours of UV irradiation, the highest concentration of five PFCAs was 0.4 nmol/L and 2.2 nmol/L, which was 1.79% and 1.02% of the initial concentration of 8:2 FTOH for 21.6 nmol/L and 216 nmol/L, respectively. Lower production rate was observed for the highest concentrations, which suggests higher production rate for longer irradiation time (> 24 hours).

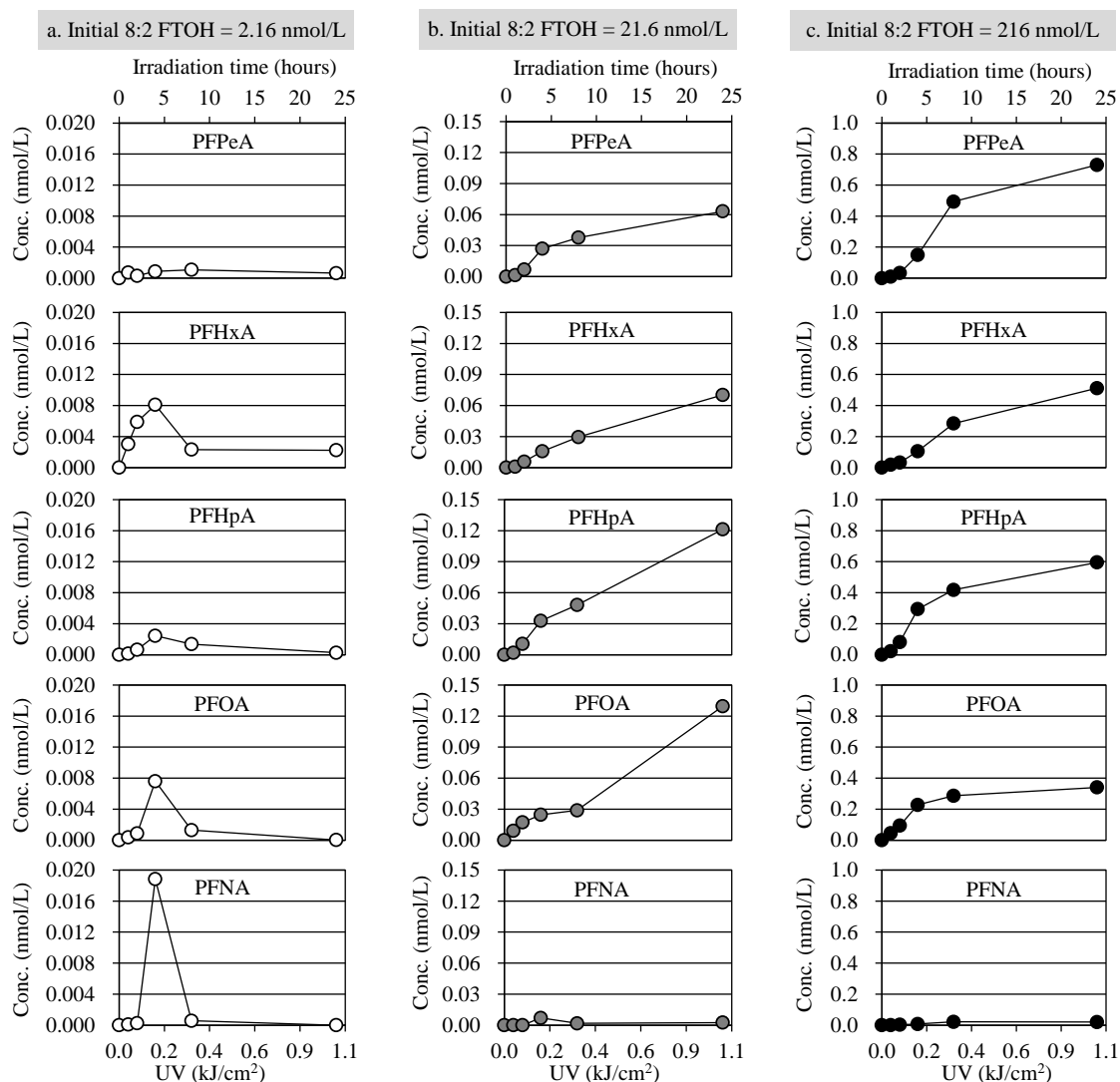


Figure 6.6 Increasing of PFCAs concentrations during UV irradiation

A series of PFCAs *i.e.* PFPeA, PFHxA, PFHpA, PFOA and PFNA were confirmed as degradation by-products of 8:2 FTOH. Among these PFCAs, PFNA (0.87%) was detected at the highest production rate for initial concentration of 2.16 nmol/L of 8:2 FTOH, whereas PFOA (0.60%) and PFHpA (0.28%) were the highest production rate compounds for the concentration of 21.6 nmol/L and 216 nmol/L, respectively.

The UV irradiation experiment showed that 8:2 FTOH was degraded at a very fast rate and completely degraded within 24 hours. However, PFCAs were gradually formed with a very slow rate and they were produced in a small portion. These results indicated that FTOHs were not immediately and directly degraded to PFCAs but some

intermediates were firstly formed and later degraded to PFCAs. Lange C. (2002) (mentioned in Dinglasan *et al.*, 2004) reported detection of 6-7% PFOA by biodegradation of fluorotelomer alcohol mixtures. Dinglasan *et al.* (2004) assessed mass balance of 8:2 FTOH, which showed that non-volatile metabolites account for 55% of biodegradation products of 8:2 FTOH. Therefore, intermediate compounds or other degradation by-products of 8:2 FTOH need to be investigated.

6.4.3 Identification of Degradation By-products of 8:2 FTOH

For identifying degradation by-products, a solvent blank sample, a control sample (0 hour irradiation) and irradiated (1-24 hours irradiation) samples for the initial concentration of 10,000 ng/L (21.6 nmol/L) of 8:2 FTOH were analysed by SCAN mode of HPLC-MS/MS. Total ion chromatogram (TIC) of the samples is shown in **Fig. 6.7**. Compared to the solvent blank and control samples, TIC peaks of irradiated samples at retention time (*RT*) up to 13 min were found after the degradation process.

Fifteen TIC peaks were clearly shown as degradation by-products of 8:2 FTOH by UV irradiation (**Fig. 6.8**). Peak 1, 4, 5 showed main compounds with the highest abundance among the others. To know these compounds, mass spectrum of each peak was checked for mass per charge (*m/z*) of ions. All mass spectrum for fifteen peaks are shown in **Figure 6.9** and the mass spectrum for each TIC peak are shown in **Appendix M**. Several *m/z* were observed as degradation by-products of 8:2 FTOH.

Figure 6.10 shows identification steps for compounds detected by SCAN mode of HPLC-MS/MS. First, *m/z* at each TIC peaks were checked. Second, possible chemical structure of the *m/z* were proposed and finally the compounds were confirmed by extracted ion chromatogram (EIC). In case of an example identification (Fig. 6.10) at *RT*=8.9, two ions (*m/z*=413 and *m/z*=369) were shown as base peak ions. These *m/z* are parent (*m/z*=413) and daughter (*m/z*=369) ions of PFOA, which was known compound and confirmed as major degradation by-products of 8:2 FTOHs by SIM mode of HPLC-MS/MS.

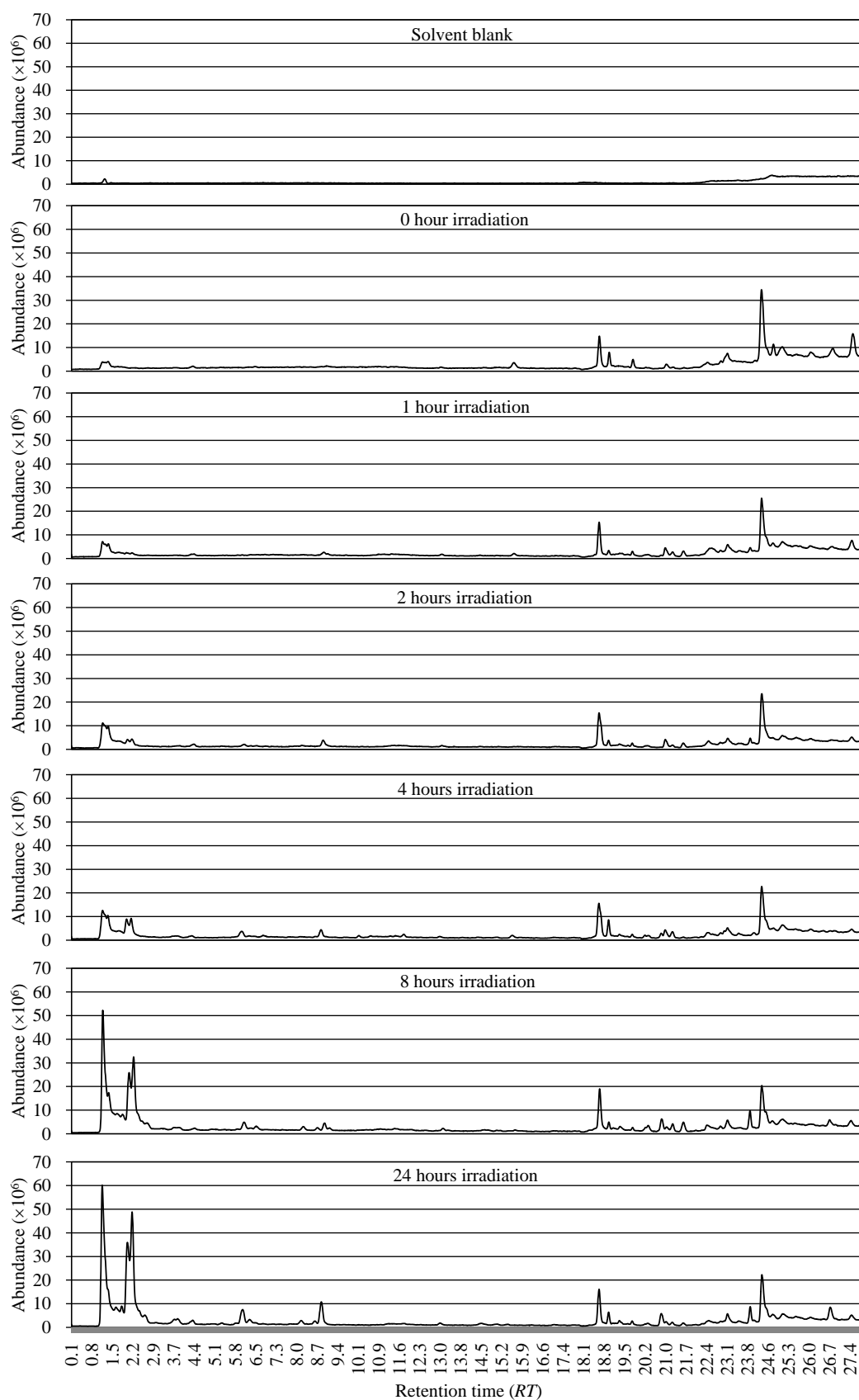


Figure 6.7 Total ion chromatograms (TIC) of solvent blank, control and irradiated samples

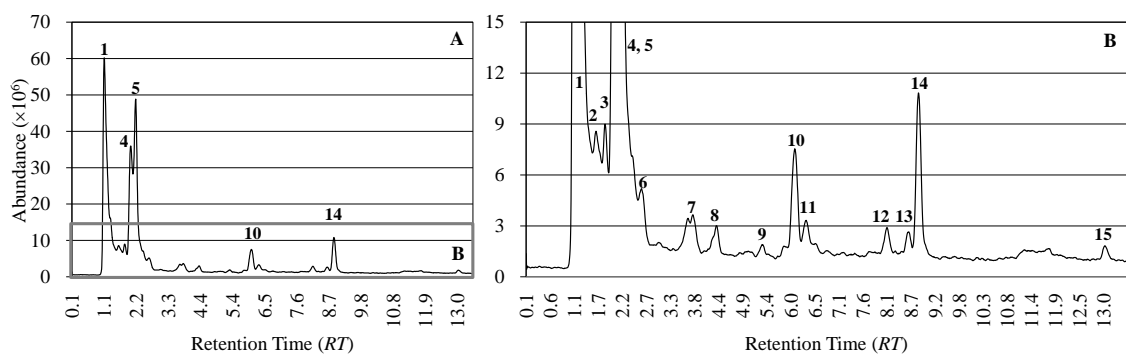


Figure 6.8 TIC peaks of 24 hours irradiated sample

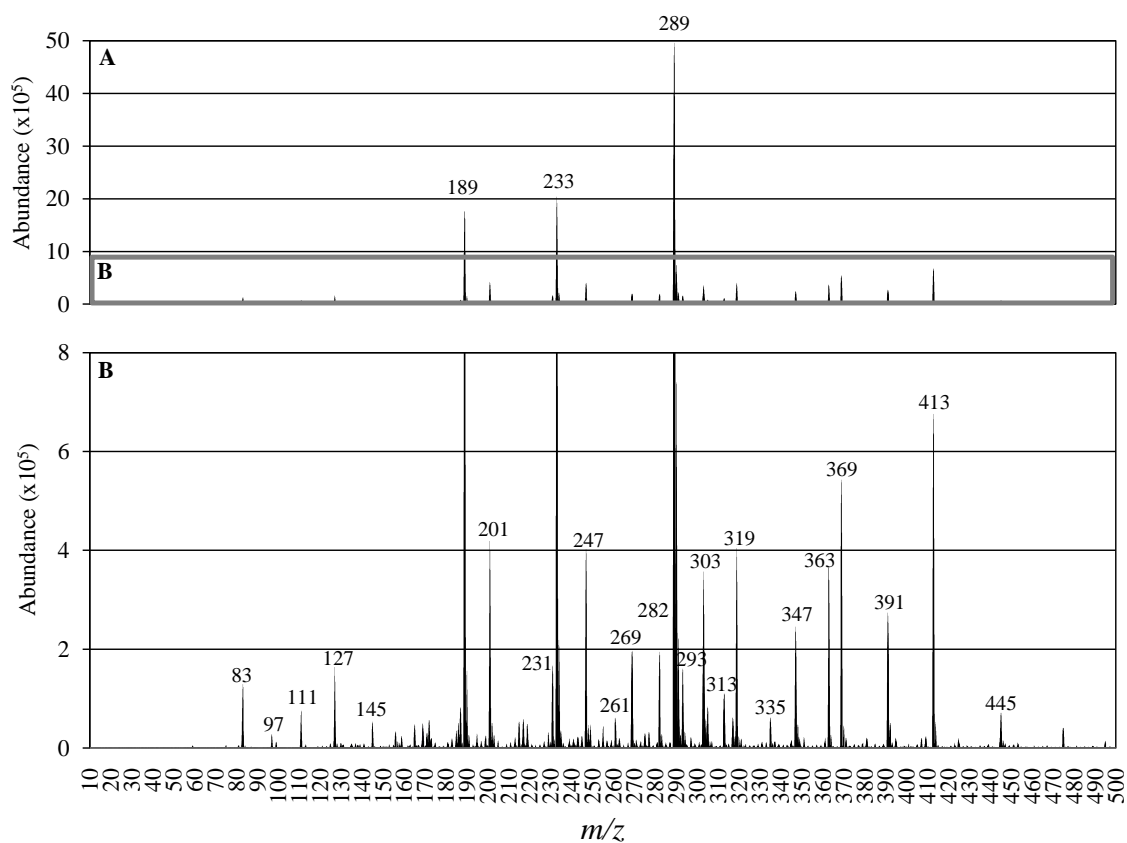


Figure 6.9 Mass spectrum (m/z) of 24 hours irradiated sample

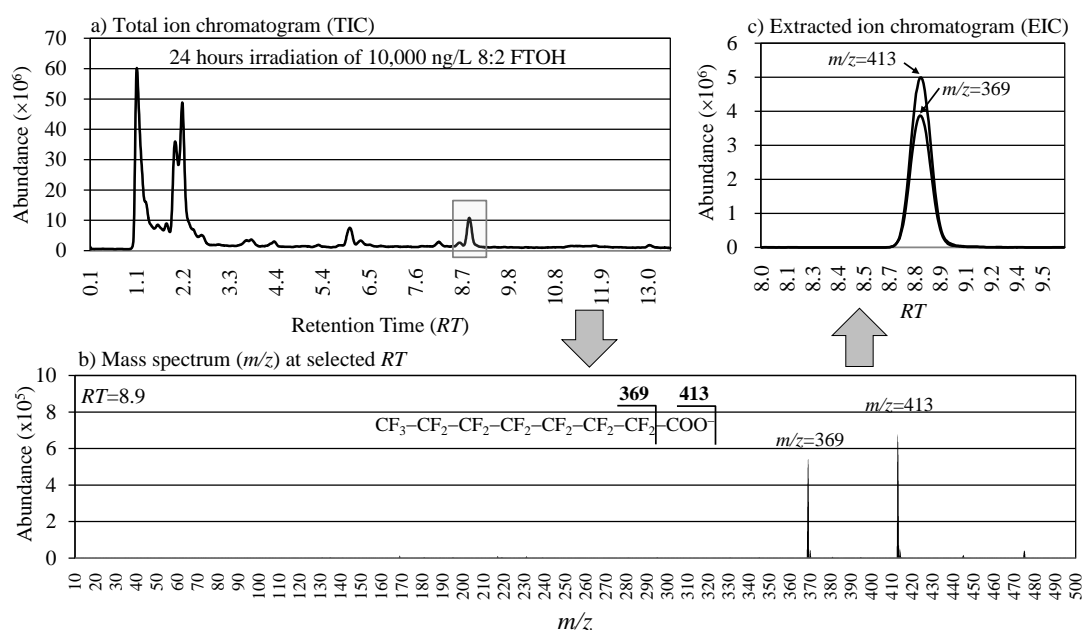


Figure 6.10 Identification of compounds by SCAN mode of HPLC-MS/MS

Table 6.4 summarizes degradation by-products of 8:2 FTOH and their corresponding fragmentation ions by SCAN mode of HPLC-MS/MS. Twenty compounds were observed as the degradation by-products. Five PFCAs (no.1-5) *i.e.* PFPeA, PFHxA, PFPeA, PFOA and PFNA were identified as the degradation products (**Fig. 6.11**), which were already confirmed by SIM mode of HPLC/MS-MS. EIC of five PFCAs are shown in **Fig. 6.11** and their abundance ranged as follows; PFOA>PFHpA>PFHxA>PFPeA>PFNA. These results concided with quantification of PFCAs by the SIM mode.

Six compounds (no. 6-11) of fluorotelomer acid (FTCAs) were identified as degradation products of 8:2 FTOH *i.e.* 1:2 FTCA, 1:3 FTCA, 3:2 FTCA, 4:2 FTCA, 4:3 FTCA and 6:3 FTCA. Two compounds (no. 12-13) of fluorotelomer unsaturated acid (FTUCAs) were identified as the degradation by-products *i.e.* 2:3 FTUCA and 4:3 FTUCA. Other seven compounds (*i.e.* $m/z = 231, 259, 282, 293, 303, 335, 445$) were also observed as degradation by-products of 8:2 FTOH. The compound with $m/z = 445$ was 8:2 fluorotelomer olefin. EIC of these degradation by-products are shown in **Fig. 6.12**

Table 6.4 Chemical structures of degradation by-products using the SCAN mode

No.	TIC	Name	Compounds <i>m/z</i>	Structures	Fragmentation ion <i>m/z</i>	Fragmentation ion structures
Perfluoroalkyl carboxylates (PFCAs)						
①	4, 5	PFPeA	263	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-COO}^-$	219	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2^-$
②	7	PFHxA	313	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-COO}^-$	269	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2^-$
③	10	PFHpA	363	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-COO}^-$	319	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2^-$
④	14	PFOA	413	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-COO}^-$	369	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2^-$
⑤	-	PFNA	463	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-COO}^-$	419	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2^-$
Fluorotelomer acids (FTCAs)						
⑥	1	1,2 FTCA	127	$\text{CF}_3\text{-CH}_2\text{-COO}^-$	111	$\text{CF}_3\text{-CH}_2\text{-CO}^-$
					83	$\text{CF}_3\text{-CH}_2^-$
⑦	1	1,3 FTCA	141	$\text{CF}_3\text{-CH}_2\text{-CH}_2\text{-COO}^-$	97	$\text{CF}_3\text{-CH}_2\text{-CH}_2^-$
					83	$\text{CF}_3\text{-CH}_2^-$
⑧	1	3,2 FTCA	227	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CH}_2\text{-COO}^-$	183	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CH}_2^-$
⑨	1	4,2 FTCA	277	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CH}_2\text{-COO}^-$	261	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CH}_2\text{-CO}^-$
					233	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CH}_2^-$
⑩	1	4,3 FTCA	291	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CH}_2\text{-CH}_2\text{-COO}^-$	247	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CH}_2\text{-CH}_2^-$
					233	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CH}_2^-$
⑪	4, 5	6,3 FTCA	391	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CH}_2\text{-CH}_2\text{-COO}^-$	347	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CH}_2\text{-CH}_2^-$
Fluorotelomer unsaturated acids (FTUCAs)						
⑫	1	2,3 FTUCA	189	$\text{CF}_3\text{-CF}_2\text{-CH=CH-COO}^-$	145	$\text{CF}_3\text{-CF}_2\text{-CH=CH}^-$
⑬	4, 5	4,3 FTUCA	289	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CH=CH-COO}^-$	-	-
Others						
⑭	1	-	231	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF=CF}^-$	-	-
⑮	1	-	259	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CHF-CH}_2\text{-COO}^-$	215	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CHF-CH}_2^-$
					201	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CHF}^-$
⑯	11	-	282	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CH}_2^-$	-	-
⑰	8, 9	-	293	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CFH-CH}_2\text{-CO}^-$	-	-
⑱	1, 2, 3	-	303	Unknown	-	-
⑲	1	-	335	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-O}^-$	-	-
⑳	15	8,2 telomer olefin	445	$\text{CF}_3\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-CH=CH}^-$	-	-

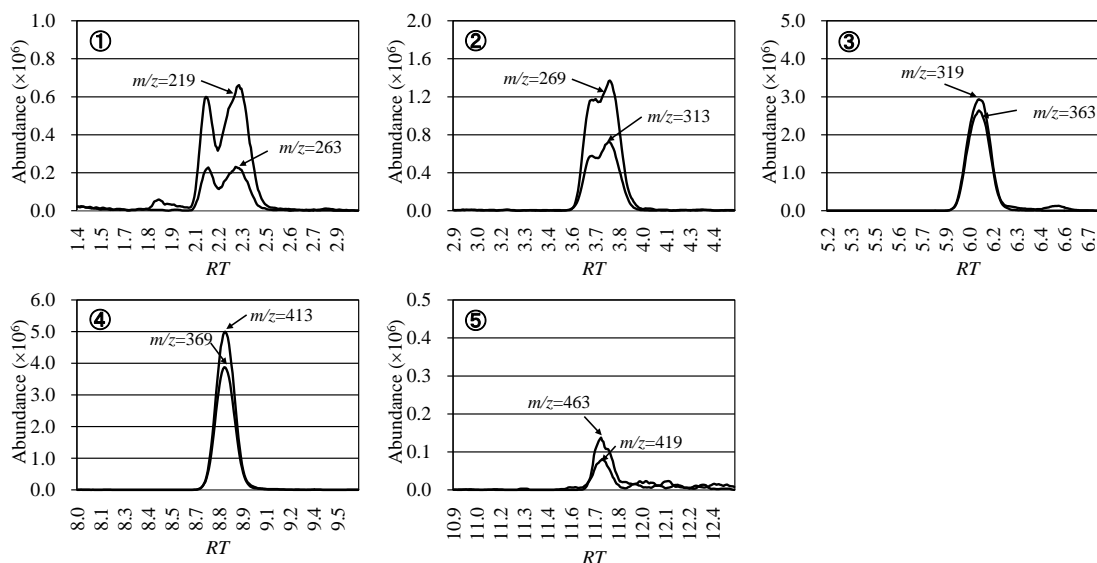


Figure 6.11 Extracted ion chromatograms of PFCAs by SCAN mode of HPLC/MS-MS

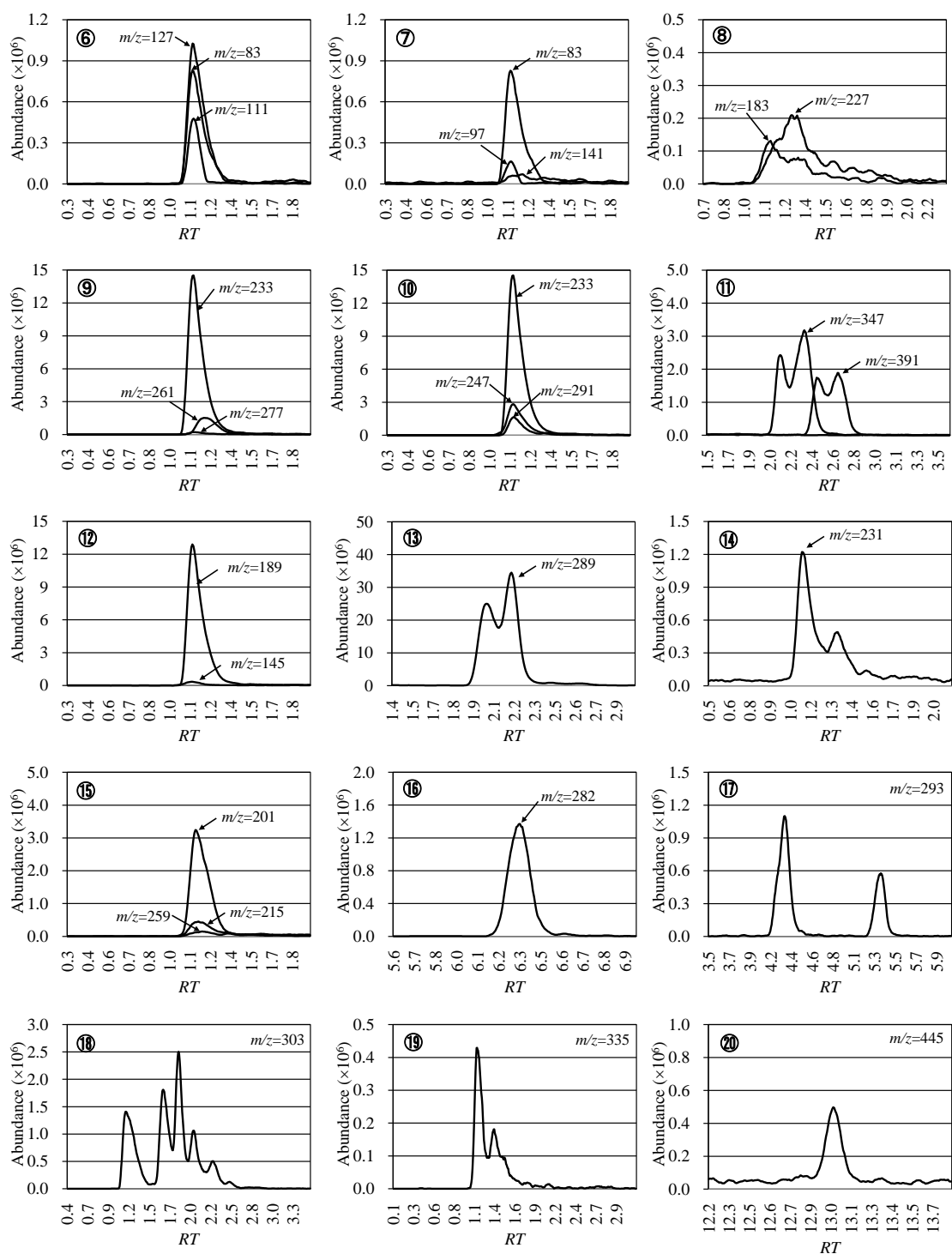


Figure 6.12 Extracted ion chromatograms of FTCAs, FTUCAs and other degradation by-products of 8:2 FTOH

6.5 Summary

8:2 FTOH was fast degraded under UV (254 nm) irradiation without any photo-catalysts. After 24 hours of irradiation, it was not detected for initial concentration of 2.16 nmol/L and 21.6 nmol/L, and remained 1.63% of the initial concentration of 216 nmol/L. First-order kinetic was used to simulate degradation of 8:2 FTOH and the rate constant was 0.228, 0.298 and 0.188 hour⁻¹ for the initial concentration of 2.16 nmol/L and 21.6 nmol/L and 216 nmol/L, respectively.

Using SIM mode of HPLC-MS/MS, five PFCAs with carbon chain length of 5 to 9 were detected as degradation by-products of 8:2 FTOH for all three initial concentrations. For the lowest initial concentration of 8:2 FTOH (2.16 nmol/L), five PFCAs increased their concentrations within 4 hours of irradiation but later decreased. Similarly, PFNA for the initial concentrations of 21.6 nmol/L and 216 nmol/L was decreased after 4 hours and 8 hours of irradiation, respectively. These decreasing indicated further degradation of PFCAs to form other per- or polyfluoroalkyl substances. Within 24 hours of UV irradiation, the highest production rate of PFCAs was 1.76%, 1.79% and 1.02% for the initial concentration of 8:2 FTOH *i.e.* 2.16 nmol/L and 21.6 nmol/L and 216 nmol/L, respectively.

Using SCAN mode of HPLC-MS/MS, twenty compounds were identified as degradation by-products of 8:2 FTOH. Five PFCAs (C5-C9) were observed and the results were consistent with the SIM mode. In addition, five FTCA *i.e.* 1:2 FTCA, 1:3 FTCA, 3:2 FTCA, 4:2 FTCA, 4:3 FTCA and 6:3 FTCA, and two FTUCAs *i.e.* 2:3 FTUCA and 4:3 FTUCA, other seven compounds were identified as the degradation products of 8:2 FTOH.

Chapter 7

Conclusions and Recommendations

7.1 Conclusions

FTOHs and PFCAs in air environment in Thailand were investigated. Air samples were collected from eight outdoor sites *i.e.* three industrial wastewater treatment plants (WWTPs), one domestic WWTP and four residential areas, and six indoor sites *i.e.* a condominium, a printing shop, two offices, a laboratory and a furniture shop. Detection of FTOHs and PFCAs at every outdoor and indoor air sampling site illustrated their contamination in the study areas. Concentrations of FTOHs (1,690-13,030 pg/m^3) were about two orders of magnitude higher than the concentrations of PFCAs (4-110 pg/m^3). Compared to the developed countries, outdoor FTOHs concentrations in Thailand were found in higher level in most of other countries, while indoor concentrations were found at the similar high levels as the developed countries. The highest outdoor concentration of FTOHs and PFCAs was found at an industrial WWTP, which indicated their sources from industrial sectors.

Possible industrial sources of airborne FTOHs and PFCAs in Japan were investigated. Very high concentrations of FTOHs and PFCAs were detected in the air at a fluorotelomer compounds production industry (588,000 pg/m^3 and 604,000 pg/m^3 , respectively). Four to five levels of magnitude of FTOHs and PFCAs in this industry were higher than those in a remote site (130 pg/m^3 and 25 pg/m^3 , respectively). Very high concentrations of FTOHs (219,000 pg/m^3) were also detected in an industry which using fluorotelomer compounds for their process. Different compounds of FTOHs and PFCAs were emitted from these industrial sources. 6:2 FTOH and PFHxA were the dominant compounds from the fluorotelomer compounds production industry whereas 8:2 FTOH and 10:2 FTOH were the dominance from the industry which using fluorotelomer compounds for their production process. In the air, FTOHs were dominant in gas-phase (77.9-100%) whereas PFCAs were mainly detected in particle-phase (73.4-99.8%).

Inhalation intakes were calculated to estimate human exposure to FTOHs and PFCAs. In Thailand, the intake of FTOHs and PFCAs (mean scenario for adult) was 0.636 ng/kg-day and 0.004 ng/kg-day, respectively. Contribution of PFOA intakes by air inhalation (1%) and dust ingestion (8%) were insignificant compared to drinking water (49%) and food consumption (42%). However, PFCAs contribution by inhalation of their precursor compounds should not be neglected for overall exposure. Total intake of PFCAs and FTOHs by four exposure pathways for Thai people was 4.909 ng/kg-day. In Japan, very high inhalation intakes of FTOHs and PFCAs were found at the fluorotelomer compounds production industry. Total intake of FTOHs and PFCAs was 206 ng/kg-day for mean scenario and 876 ng/kg-day for worst scenario, which exceeded recommendation guideline by Japanese government (300 ng/kg-day). Air cleaner with activated carbon fiber filter was applied in this industry to remove FTOHs and PFCAs at the emission point sources. Higher reduction rates were observed for FTOHs (48-88%), compared to PFCAs (3-53%).

Rainwater and air samples were collected at Kyoto, Japan in order to investigate wet deposition of FTOHs and PFCAs from the air. All PFCAs (C5-C9) were detected in every rainwater (7.3-28.7 ng/L) and air (90-190 pg/m³) sample, which indicated distribution of PFCAs from air to water environment. PFCAs in rainwater were dominant in liquid-phase (71-92%); however, solid-phase partitioning increased with increasing of fluorocarbon chain length. Total amount of precipitation during sampling period was 8.1-250.5 mm and total flux of PFCAs ranged between 120-1,830 ng/m². Total annual precipitation in Kyoto in 2013 was 1,450.5 mm and estimated annual flux of PFCAs was 21,900 ng/m². FTOHs were detected in air samples (770-2,820 pg/m³) but the concentrations in rainwater samples were below detection limits (<6.9-8.7 ng/L). Therefore, FTOHs might be difficult to be wet deposited from the air. Most of PFCAs in rainwater increased after a few weeks of sunlight exposure. Increasing rates ranged between 18-186%. These results suggested photodegradation of their precursor compounds. Increasing of PFCAs (9-373%) in river water was also found in Chao Praya River, Thailand, which confirmed potential PFCAs by degradation of their precursor compounds in water environment.

To elucidate contribution of FTOHs to PFCAs in water environment, photodegradation experiment was conducted using an UV (254 nm) reactor. Three initial concentrations *i.e.* 1,000 ng/L (2.16 nmol/L), 10,000 ng/L (21.6 nmol/L) and 100,000 ng/L (216 nmol/L) of 8:2 FTOH solutions were prepared in *ultrapure* water. 8:2 FTOH was fast degraded under UV light without any catalysts. After 24 hours of irradiation, it was not detected for the initial concentration of 2.16 nmol/L and 21.6 nmol/L, and remained 1.63% of the initial concentration of 216 nmol/L. First-order kinetic was used to simulate degradation of 8:2 FTOH and the rate constants were 0.228, 0.298 and 0.188 hour⁻¹ for the initial concentration of 2.16 nmol/L and 21.6 nmol/L and 216 nmol/L, respectively. Five PFCAs with carbon chain length of 5 to 9 were formed as degradation by-products of 8:2 FTOH for all three initial concentrations. Within 24 hours of UV irradiation, the highest formation rate of PFCAs was 1.76%, 1.79% and 1.02% for the initial concentration of 8:2 FTOH *i.e.* 2.16 nmol/L and 21.6 nmol/L and 216 nmol/L, respectively. Not only PFCAs but also other compounds were identified as degradation by-products of 8:2 FTOH using SCAN mode of HPLC-MS/MS. These compounds include fluorotelomer acids (FTCAs), fluorotelomer unsaturated acids (FTUCAs) and fluorotelomer olefins.

7.2 Recommendations

The study results indicated contamination of FTOHs and PFCAs in air environment and their contribution to water environment. The followings are remaining issues for future research based on this study;

1. Identification of possible sources of FTOHs from commercial products
2. Implementation of countermeasures for removal of FTOHs and PFCAs from the industrial point sources in Japan
3. Further study on degradation mechanism and pathways of FTOHs in air
4. Further study on UV irradiation of FTOHs by continuous experiment, their mass balance and quantification of their by-products
5. Further study on contribution of PFCAs from other precursor compounds
6. Development analytical method with higher sensitivity for FTOHs in water samples

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Appendix A

Review of FTOHs and PFCAs in Air Environment

A1. Review of FTOHs concentration in outdoor and indoor air from previous studies

Sampling sites country (city)/ locations	Year	n	Concentration (pg/m ³)				Reference
			6:2FTOH	8:2FTOH	10:2FTOH	ΣFTOH	
<u>Outdoor sites</u>							
Japan sea to the Arctic Ocean	2010	13	4.0 (0.9-12.1)	141 (53-289)	22 (6.2-48)	167 (64-349)	Cai <i>et al.</i> , 2012
Canada (Ontario)/ Aeration tank at a WWTP	2010	12	5,708	4,710	928	11,025	Vierke <i>et al.</i> , 2011
Korea (Seoul, Ansan/Shiheung, Daegu)/ Nationwide	2009	6	- -	9,346 (<44.7-19,553)	10,125 (62-25,981)	19,471 (107-50,119)	Kim <i>et al.</i> , 2012
Canada (Vancouver)/ House's yard	2007-2008	6	128 (51-388)	186 (83-367)	71 (27-153)	385 (161-906)	Shoeib <i>et al.</i> , 2011
The Atlantic-Southern Oceans/ Ship-based samples	2007-2008	140	6.3	19	6.4	32	Dreyer <i>et al.</i> , 2009
The Northeast Atlantic Ocean/ - Ship-based samples	2007	11	10 (0.1-41)	43 (2.3-190)	21 (2.9-76)	74 (6.3-306)	Shoeib <i>et al.</i> , 2010
- Bermuda/ Background site	2007	7	3.0 (1.9-4.9)	21 (7.9-30)	10 (7.4-15)	34 (18-47)	
Japan/ - Keihan area	2007	19	<15	179	63	250	Oono et al., 2008a
- Across Japan	2007	15	222	441	53	716	
Japan (Keihan area)	2006	24	35 (7-170)	1,192 (48-4,585)	136 (8-518)	1,363 (63-5,005)	Oono <i>et al.</i> , 2008b
UK (Hazelrigg)/ Semi-rural	2005-2006	10	32	75	21	128	Barber <i>et al.</i> , 2007
UK (Manchester)/ Urban	2005	4	125	240	65	430	
Ireland (Mace Head)/ Rural	2005	4	5.1	12.3	8.1	25	Barber <i>et al.</i> , 2007

A1. Review of FTOHs concentration in outdoor and indoor air from previous studies (Cont.)

Sampling sites country (city)/ locations	Year	n	Concentration (pg/m ³)				Reference
			6:2FTOH	8:2FTOH	10:2FTOH	ΣFTOH	
Germany (Hamburg)/Urban area	2005	7	66 (33-149)	119 (62-275)	35 (16-93)	208 (94-462)	Jahnke <i>et al.</i> , 2007b
Germany (Waldhof)/Rural area	2005	4	64 (17-125)	75 (33-112)	23 (10-32)	162 (60-269)	Jahnke <i>et al.</i> , 2007b
The Arctic atmosphere/ Ship-based sample	2005	20	2.7 (<1.1-6.0)	14.9 (5.8-26)	7.1 (1.9-17)	25 <i>n.a.</i>	Shoeib <i>et al.</i> , 2006
North American Troposphere	2001						Stock <i>et al.</i> , 2004
- U.S. (Griffin, Georgia)/ Point source site		5	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	148	
- U.S. (Clevs, Ohio)/ Sub-urban		3	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	132	
- U.S. (Reno, Nevada)/ Sub-urban		3	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	76	
- Canada (Long Point, Ontario)/ Rural		3	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	26	
- Canada (Toronto, Ontario)/ Urban		3	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	165	
- Canada (Winnipeg, Minitoba)/ Isolated site		3	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>	11	
<u>Indoor sites</u>							
Germany/ House	2009-2010	4	2,098	13,283	3,637	19,017	Langer <i>et al.</i> , 2010
Germany/ Office	2009-2010	3	4,522	4,919	1,621	11,062	Langer <i>et al.</i> , 2010
Germany/ Printing shop	2009-2010	4	2,811	34,107	1,619	38,133	Langer <i>et al.</i> , 2010
Germany/ Furniture shop	2009-2010	4	18,128	86,964	23,381	128,473	Langer <i>et al.</i> , 2010
Korea (Seoul, Ansan-Shiheung, Daegu)/ House	2009	7	-	4,839	2,610	7,449	Kim <i>et al.</i> , 2012
			-	(2,317-7,801)	(972-4,564)	(3,531-95,378)	
Japan (Keihan area)/ House	2008	84	590 (<60-12,090)	10,160 (360-63,020)	2,290 (<70-13,000)	13,040 <i>n.a.</i>	Liu <i>et al.</i> , 2013
Canada (Vancouver)/ House	2007-2008	59	2,440 (<7.5-22,890)	3,790 (660-16,080)	1,420 (220-8,160)	7,740 (889-47,130)	Shoeib <i>et al.</i> , 2011
Norway / House	2007-2008	6	96	8,790	3,575	12,460	Huber <i>et al.</i> , 2011
Norway/ Office	2007-2008	1	266	3,151	1,970	5,387	Huber <i>et al.</i> , 2011
Norway / House	2008	40	1,492	6,438	4,088	12,018	Haug <i>et al.</i> , 2011
Norway (Tromsø)/ House	2005	4	2,990	3,424	3,572	9,986	Barber <i>et al.</i> , 2007

Note: *n.a.* = not available, – = not measure, ΣFTOH = 6:2 FTOH+8:2 FTOH+10:2 FTOH

A2. Review of PFCAs concentration in outdoor and indoor air from previous studies

Sampling sites country (city)/ locations	Year	n	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	ΣPFCAs	Reference
<u>Outdoor sites</u>												
Canada (Ontario)/ Aeration tank at a WWTP	2010	12	31	72	23	84	23	47	15	1.3	297	Vierke <i>et al.</i> , 2011
Canada (Vancouver)/ House's yard	2007-2008	6	-	<0.02	1.7	2.5	<0.02	1.4	<0.02	<0.02	6	Shoeib <i>et al.</i> , 2011
			-	(<0.02)	(<0.33-2.5)	(<0.47-9.2)	(<0.02)	(<0.02-6.1)	(<0.02)	(<0.02)	(<0.6-35)	
The Atlantic-Southern Oceans/ Ship-based samples	2007-2008	140	0.1	0.2	0.2	0.7	0.3	0.2	0.1	0.1	2	Dreyer <i>et al.</i> , 2009
UK (Hazelrigg)/ Semi-rural	2005-2006	10	-	107	1.6	101	0.9	1.0	0.7	<0.01	212	Barber <i>et al.</i> , 2007
UK (Manchester)/ Urban	2005	4	-	<26	8.2	341	<26.6	5.4	<0.01	<0.01	381	
Ireland (Mace Head)/ Rural	2005	4	-	<13.8	<0.001	8.9	<3.3	<2.8	<0.002	<0.003	19	Barber <i>et al.</i> , 2007
<u>Indoor sites</u>												
Canada (Vancouver)/ House	2007-2008	59	-	25	10	113	89	49	3.4	9.8	299	Shoeib <i>et al.</i> , 2011
			-	(<0.02-205)	(<0.33-69)	(<0.47-2,570)	(<0.02-2,166)	(<0.02-977)	(<0.02-79)	(<0.02-263)		
Norway (Tromsø)/ House	2005	4	-	17.1	0.8	4.4	2.7	3.4	<1.3	1.2	30	Barber <i>et al.</i> , 2007

Note: n.a. = not available, – = not measure, ΣPFCAs = PFPeA+PFHxA+PFHpA+PFOA+PFNA+PFDA+PFUnDA+PFDoDA

Appendix B

Review of Sampling and Analytical Methods of FTOHs and PFCAs in Air Samples

Reference	Sites	Sampler	Flow rate (L/min)	Sampling media	Compounds	Extraction (solvent)	Concentration	Cleanup
Jogsten <i>et al.</i> , 2012	Indoor	Personal pump	0.002	SPE Envi+ Cartridge	FTOHs (g+p)	Soaking&sonication (MeOH)	Rotary evaporator/ N ₂	-
	Outdoor	High volume	~210-235	PUF/XAD-2/PUF	FTOHs (g)/ PFCAs (g)	Soaking&sonication (MeOH)	Rotary evaporator/ N ₂	-
				QFFs	FTOHs (p)/ PFCAs (p)	Soaking&sonication (MeOH)	Rotary evaporator/ N ₂	-
Cai <i>et al.</i> , 2012	Outdoor	High volume	~174	PUF/XAD-2	FTOHs (g)	Soxhlet apparatus (DCM/hexane)	Rotary evaporator	Na ₂ SO ₄
				GFF	FTOHs (p)	Soxhlet apparatus (DCM)	Rotary evaporator	Na ₂ SO ₄
Kim <i>et al.</i> , 2012	Indoor/	Passive air	-	PUF disks/ SIP disks	FTOHs (g+p)	Soxhlet apparatus (PE/acetone)	Rotary evaporator/ N ₂	-
	Outdoor	Low volume	~2.1	PUF/XAD	FTOHs (g+p)	Soxhlet apparatus (PE/acetone)	Rotary evaporator/ N ₂	-
Vierke <i>et al.</i> , 2011	Outdoor	High volume	~97	PUF/XAD-2/PUF	FTOHs (g)	Soxhlet apparatus (PE)	Rotary evaporator/ N ₂	Na ₂ SO ₄
					PFCAs (g)	Soxhlet apparatus (MeOH)	Rotary evaporator/ N ₂	Envi-Carb
				GFF	FTOHs (p)	Sonication (DCM)	Rotary evaporator/ N ₂	Na ₂ SO ₄
					PFCAs (p)	Sonication (MeOH)	Rotary evaporator/ N ₂	Envi-Carb
Haug <i>et al.</i> , 2011; Dreyer <i>et al.</i> , 2009	Indoor	Personal pump	0.004	PUF/XAD-2/PUF	FTOHs (g+p)	Soaking&sonication (EtOAc)	Turbo Vap evaporator/ N ₂	cotton/ ENVI-Carb
Langer <i>et al.</i> , 2010	Indoor	Passive air	-	SIP disks	FTOHs (g+p)	FBE (acetone/MTBE)	Rotary evaporator/ N ₂	-
Dreyer <i>et al.</i> , 2009	Outdoor	High volume	~313	PUF/XAD-2/PUF	FTOHs (g)	FBE (MTBE/acetone)	<i>n.a.</i>	-
				GFFs	FTOHs (p)	FBE (MTBE/acetone)	<i>n.a.</i>	-
					PFCAs (p)	FBE (MeOH)	<i>n.a.</i>	-
Dreyer and Ebinghaus, 2009	Outdoor	High volume	~243	PUF/XAD-2/PUF	FTOHs (g)	Soaking (EtOAc)	Rotary evaporator/ N ₂	-
				GFFs	FTOHs (p)	Fluidized bed (acetone/MTBE)	Rotary evaporator/ N ₂	-
				GFFs	PFCAs (p)	Fluidized bed (MeOH)	Rotary evaporator/ N ₂	-
Oono <i>et al.</i> , 2008	Outdoor	High volume	700	PUF/ACF	FTOHs (g)	Soaking (EtOAc)	Rotary evaporator/ N ₂	Na ₂ SO ₄ / silica gel
				QFF	FTOHs (p)	Soaking (EtOAc)	Rotary evaporator/ N ₂	Na ₂ SO ₄ / silica gel

Reference	Sites	Sampler	Flow rate (L/min)	Sampling media	Compounds	Extraction (solvent)	Concentration	Cleanup
Oono et al., 2008	Outdoor	Passive air	-	ACF	FTOHs (g+p)	Soaking (EtOAc)	Rotary evaporator/ N ₂	Na ₂ SO ₄
Loewen et al., 2008	Outdoor	Passive air	-	XAD-2	FTOHs (g+p)	Soaking (EtOAc)	Rotary evaporator/ N ₂	diatomaceous earth
Jahnke et al., 2007	Outdoor	High volume	200-300	PUF/XAD-2/PUF	FTOHs (g)	Cold column elution (EtOAc)	Rotary evaporator	-
				GFFs	FTOHs (p)	Shaking (EtOAc)	Rotary evaporator/ N ₂	-
				GFFs	PFCAs (p)	Ultrasonic (MeOH)	RapidVap evaporator/ N ₂	cotton wool
Kim and Kannan, 2007	Outdoor	High volume	500-600	PUF/XAD-2/PUF	FTOHs (g)/ PFCAs (g)	Shaking (EtOAc/ MeOH)	Rotary evaporator/ N ₂	-
				QFFs	FTOHs (p)/ PFCAs (p)	Shaking and sonication (MeOH)	Rotary evaporator/ N ₂	-
Piekarz et al., 2007	Outdoor	High volume	~417-556	PUF	FTOHs (g)	ASE (EtOAc/DCM)	Turbovap evaporator/ N ₂	-
				XAD-2	FTOHs (g)	ASE (hexane/acetone)	Turbovap evaporator/ N ₂	-
				QFFs	FTOHs (p)	ASE (EtOAc/DCM)	Turbovap evaporator/ N ₂	-
				QFFs	PFCAs (p)	ASE (EtOAc/DCM)	Turbovap evaporator/ N ₂	-
Jahnke et al., 2007	Outdoor	High volume	200-250	PUF/XAD-2/PUF	FTOHs (g)	Cold column elution (EtOAc)	n.a.	-
				GFFs	FTOHs (p)	Soaking&shaking (EtOAc)	n.a.	-
Shoeib et al., 2006	Outdoor	High volume	~208	PUF/XAD-2/PUF	FTOHs (g)	Soxhlet apparatus (PE/acetone)	Rotary evaporator/ N ₂	alumina gel
				GFF	FTOHs (p)	Soxhlet apparatus (DCM)	Rotary evaporator/ N ₂	-
Stock et al., 2004	Outdoor	High volume	200-400	PUF/XAD-2/PUF and QFFs	FTOHs (g+p)	Soaking (MeOH/ EtOAc)	Rotary evaporator/ N ₂	Na ₂ SO ₄ / syringe filters

Note: n.a. = not available, (g) = gas-phase, (p) = particle-phase, DCM = dichloromethane, PE = petroleum ether, EtOAc = ethyl acetate, MTBE = methyl tetra butyl ether, MeOH= methanol, ASE = Accelerated solvent extraction, FBE = Fluidized bed extraction, Na₂SO₄ = sodium sulfate

Appendix C

Review of Method and Parameters for Calculation of Intake of FTOHs and PFCAs

Calculation of daily intakes of PFCAs and FTOHs is shown in following equation and variables in the equation are explained in **Table C1**. Review of parameters, which was used for the calculation, is summarized in **Table C2**.

$$I = \frac{C \times Q \times F_{uptake} \times T}{BW}$$

C1. Variables in equation for calculation of daily intakes

Parameters	Air	Dust	Food	Drinking water
Daily intakes (I)	ng/kg-day	ng/kg-day	ng/kg-day	ng/kg-day
Concentrations in environmental media (C)	C_{air} (ng/m ³)	C_{dust} (ng/g)	C_{food} (ng/g)	C_{water} (ng/L)
Daily consumption (Q)	Q_{air} (m ³ /day)	Q_{dust} (g/day)	Q_{food} (g/day)	Q_{water} (L/day)
Uptake fraction (F_{uptake})	unitless	unitless	unitless	unitless
Time factors (T)	unitless	unitless	unitless	unitless
Body weight (BW)	kg	kg	kg	kg

C2. Summary of parameters for exposure of PFCAs and FTOHs

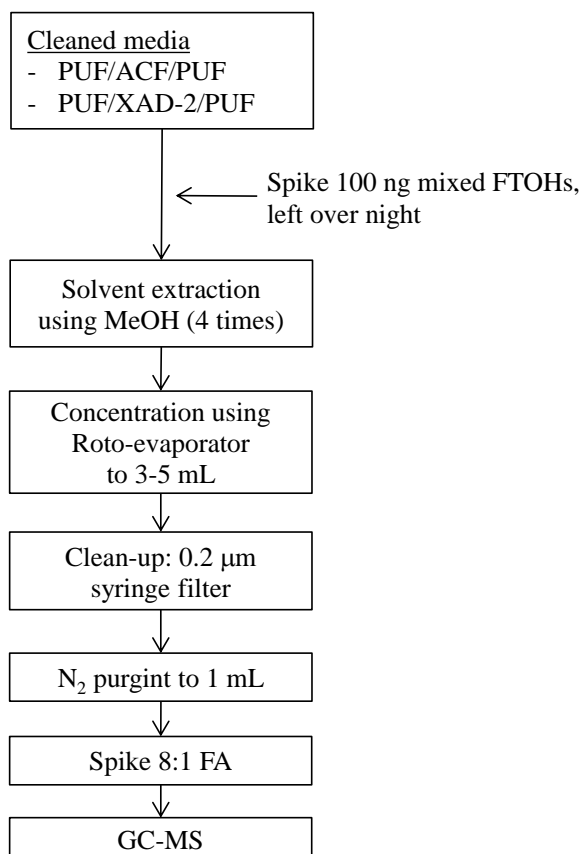
Parameters	Criteria/scenarios		Values	References
Daily inhalation volume (Q_{air})	Adult		14.6 m ³ /day	Jogsten <i>et al.</i> , 2012
			24 m ³ /day	Shoeib <i>et al.</i> , 2011
	Children		9.3 m ³ /day	Jogsten <i>et al.</i> , 2012
			15 m ³ /day	Shoeib <i>et al.</i> , 2011
Dust ingestion rate (Q_{dust})	Adult	- mean	4.16 mg/day	Shoeib <i>et al.</i> , 2011
			50 mg/day	Jogsten <i>et al.</i> , 2012; Fromme <i>et al.</i> , 2009
		- worst	55 mg/day	Shoeib <i>et al.</i> , 2011
			110 mg/day	Jogsten <i>et al.</i> , 2012
	Children	- mean	100 mg/day	Shoeib <i>et al.</i> , 2011
			68 mg/day	Jogsten <i>et al.</i> , 2012
		- worst	200 mg/day	Shoeib <i>et al.</i> , 2011
			224 mg/day	Jogsten <i>et al.</i> , 2012
Drinking water consumption (Q_{water})	Adult		1.41 L/day	Josten <i>et al.</i> , 2012; Haug <i>et al.</i> , 2011
			1.3 L/day	Fromme <i>et al.</i> , 2009
	Children		0.4 L/day	Josten <i>et al.</i> , 2012; Haug <i>et al.</i> , 2011
Uptake fraction (F_{uptake} , unitless)	FTOHs	- mean	0.38	Fasano <i>et al.</i> , 2006;
		- worst	1.00	Shoieb <i>et al.</i> , 2011;
	PFCAs	- mean	0.80	Jogsten <i>et al.</i> , 2012
		- worst	1.00	
Time spends (T , %)	indoor		90%	Jogsten <i>et al.</i> , 2012;
	outdoor		10%	Fromme <i>et al.</i> , 2009

Appendix D

Analytical Method Development for Air Samples in This Study

D1. Method recovery for FTOHs

(1) Experimental procedures

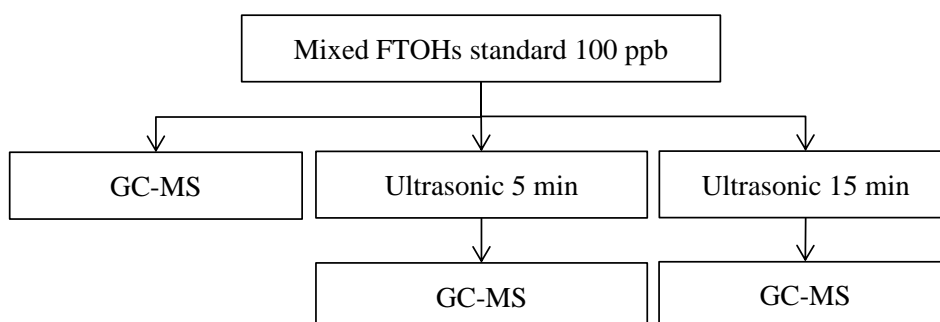


(2) Results (% recovery, average±standard deviation)

Sampling media	<i>n</i>	6:2 FTOH	8:2 FTOH	10:2 FTOH
<i>Spike 100 ng FTOHs</i>				
PUF/ACF/PUF	3	86.1±0.4	95.9±3.1	98.8±4.1
PUF/XAD-2/PUF	3	87.8±8.3	95.4±5.2	98.6±10.1
<i>Spike 1,000 ng FTOHs</i>				
PUF/ACF/PUF	2	97.9±4.4	92.6±6.6	81.2±5.8
PUF/XAD-2/PUF	3	102.0±4.2	100.4±6.3	94.4±5.6

D2. Ultrasonic test

(1) Experimental procedures

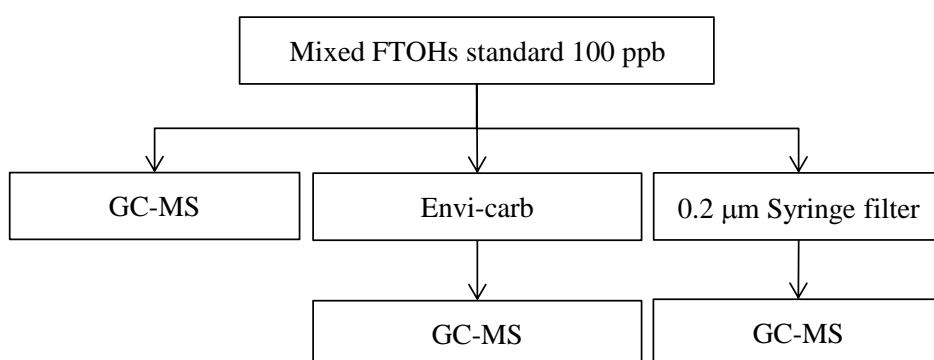


(2) Results (% recovery, average \pm standard deviation)

Ultrasonic time	<i>n</i>	6:2 FTOH	8:2 FTOH	10:2 FTOH
0 min	3	97.7 \pm 3.1	96.1 \pm 2.9	92.4 \pm 4.7
5 min	3	93.3 \pm 5.9	92.4 \pm 5.7	91.4 \pm 7.6
15 min	3	88.7 \pm 4.5	85.2 \pm 5.6	84.2 \pm 4.4

D3. Cartridge test

(1) Experimental procedures

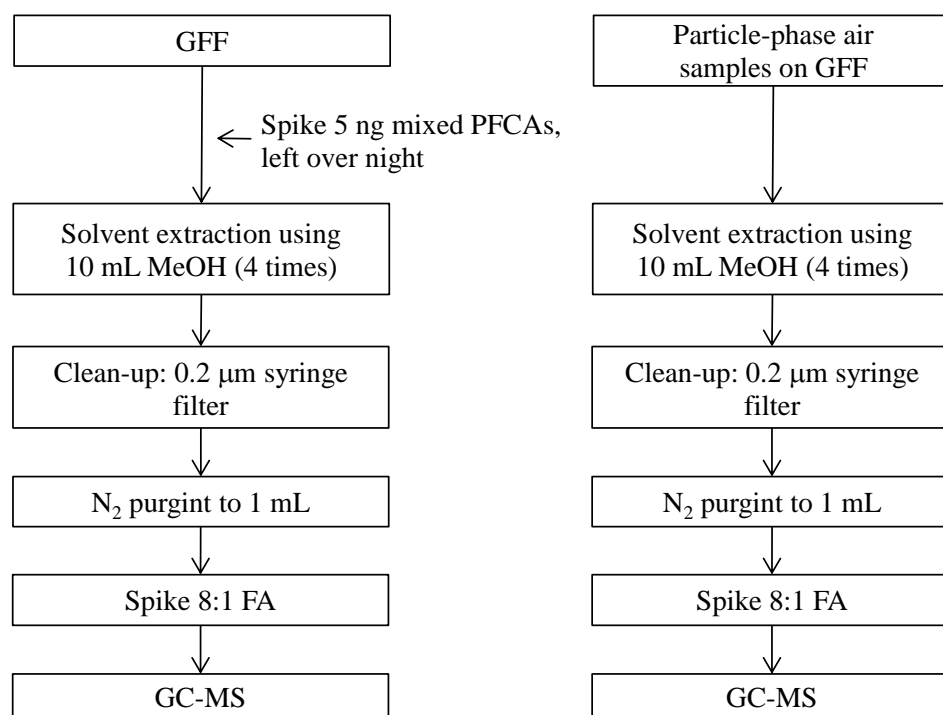


(2) Results (% recovery, average \pm standard deviation)

Cartridge types	<i>n</i>	6:2 FTOH	8:2 FTOH	10:2 FTOH
No	4	103.2 \pm 7.7	100.8 \pm 8.2	100.5 \pm 8.2
Envi-carb	4	88.6 \pm 2.7	85.6 \pm 3.6	84.3 \pm 3.2
Syringe filter	4	104.4 \pm 3.0	101.4 \pm 3.8	102.6 \pm 4.1

D4. Method recovery for particulate PFCAs

(1) Experimental procedures



(2) Results

(2.1) Recovery (% , average±standard deviation) by spiking FTOHs onto GFFs (*n*=3)

Round (R)	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
R1	62.7±9.2	103.8±12.9	94.9±6.0	92.7±3.7	114.1±5.6	102.3±2.9	113.4±4.8	93.7±3.2
R2	7.1±1.1	17.9±8.4	14.8±1.7	16.3±0.3	20.9±1.7	18.6±1.3	19.5±1.7	18.5±2.3
R3	0.3±0.7	4.0±0.00	1.4±0.2	2.1±0.8	3.0±1.3	1.5±0.2	0.8±0.1	1.1±0.1
R4	0.4±0.5	3.4±0.2	1.5±0.7	2.4±0.8	1.8±0.7	<i>n.d.</i>	<i>n.d.</i>	0.2±0.1

(2.2) Recovery (% , average±standard deviation) for PFCAs in air samples (*n*=3)

Round (R)	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
R1	90.6±2.7	88.5±3.5	90.8±3.5	90.3±2.9	89.6±2.1	88.2±2.3	88.4±1.5	84.1±1.5
R2	7.5±2.9	7.5±4.0	7.8±3.5	8.3±2.9	9.0±2.2	10.3±2.2	10.4±1.4	13.8±1.4
R3	1.4±0.3	3.2±0.6	1.2±0.2	1.2±0.1	1.2±0.2	1.3±0.2	1.1±0.1	1.7±0.3
R4	0.5±0.2	0.7±0.2	0.2±0.1	0.2±0.03	0.2±0.02	0.2±0.01	0.1±0.01	0.4±0.1

Appendix E

Concentrations of FTOHs, PFCAs and TPM in Air in Thailand

E1. Concentrations of FTOHs (pg/m³), PFCAs (pg/m³) and TPM (mg/m³) in air in Thailand for first survey

Sampling sites	Sampling date (Year 2012)	6:2 FTOH		8:2 FTOH		10:2 FTOH		PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDODA	TPM
		c(g)	c(p)	c(g)	c(p)	c(g)	c(p)	c(p)	c(p)	c(p)	c(p)	c(p)	c(p)	c(p)	c(p)	
Outdoor air																
WWTP1	October 8-9	610	n.d.	5,780	n.d.	5,460	n.d.	1.43	5.45	10.44	58.97	22.92	9.04	2.44	n.d.	0.075
WWTP2	October 15-16	340	n.d.	760	n.d.	1,830	n.d.	1.73	1.14	1.02	2.78	6.61	8.55	11.74	n.d.	0.088
WWTP3	October 22-23	270	n.d.	910	n.d.	510	n.d.	1.08	26.73	0.85	12.03	2.70	5.39	4.56	n.d.	0.042
WWTP4	September 24-25	290	n.d.	2,380	70	2,820	70	0.63	3.18	2.18	5.96	3.52	2.06	1.17	n.d.	0.045
RA1	October 4-5	220	n.d.	250	30	1,500	n.d.	1.20	6.64	1.63	6.84	1.95	1.29	0.48	n.d.	0.046
RA2	September 27-28	400	n.d.	460	20	1,660	290	0.68	1.74	0.85	3.04	n.d.	0.69	0.74	n.d.	0.125
RA3	September 30 to October 1	660	n.d.	460	n.d.	1,900	n.d.	0.74	1.67	0.69	2.74	1.39	0.84	0.96	n.d.	0.066
RA4	September 10-11	110	n.d.	790	n.d.	860	70	0.56	2.60	2.12	12.81	1.18	1.28	1.58	n.d.	0.068
Indoor air																
Condominium	October 18-19	1,570	n.d.	2,560	n.d.	8,860	40	0.70	3.13	0.85	1.41	0.89	0.28	0.36	n.d.	0.013
Printing shop	September 17-18	660	n.d.	1,770	n.d.	7,310	330	1.98	1.78	1.78	8.68	4.46	1.17	1.05	n.d.	0.050
Offiice1	October 28-29	4,520	n.d.	2,390	n.d.	2,460	20	0.65	0.74	0.54	1.13	0.63	0.29	n.d.	n.d.	0.040
Office2	September 14-15	1,260	n.d.	3,930	40	1,960	70	2.03	14.86	3.24	15.41	0.19	1.25	0.96	n.d.	0.021
Laboratory	September 12-13	340	n.d.	680	n.d.	2,080	40	0.90	4.04	2.33	31.08	3.83	0.79	0.79	n.d.	0.020
Furniture shop	September 20-21	860	n.d.	520	n.d.	1,040	90	0.90	4.77	1.86	6.89	2.90	0.85	1.11	n.d.	0.065

Note: c(g) = concentration in gas-phase, c(p) = concentration in particle-phase, *n.d.* = not detected

E2. Concentrations of FTOHs (pg/m³), PFCAs (pg/m³) and TPM (mg/m³) in air in Thailand for second survey

Name	Sampling date	6:2 FTOH		8:2 FTOH		10:2 FTOH		PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDODA	TPM
		c(g)	c(p)	c(g)	c(p)	c(g)	c(p)	c(p)	c(p)	c(p)	c(p)	c(p)	c(p)	c(p)	c(p)	
WWTP1(1)	January 10-11, 2013	640	14	7,200	18	7,940	17	2.78	7.27	44.94	45.52	16.34	15.07	2.39	0.67	0.085
WWTP1(2)	January 11-12, 2013	710	<i>n.d.</i>	7,840	<i>n.d.</i>	7,110	<i>n.d.</i>	3.02	7.01	26.25	61.35	21.40	18.98	4.20	1.37	0.080
WWTP1(3)	January 12-13, 2013	510	<i>n.d.</i>	7,550	17	6,670	15	3.53	6.72	29.72	52.05	18.74	17.02	4.54	1.52	0.078
WWTP1(4)	January 13-14, 2013	760	<i>n.d.</i>	5,400	<i>n.d.</i>	6,970	<i>n.d.</i>	3.03	6.18	43.56	56.86	21.85	21.36	6.40	1.86	0.056
WWTP1(5)	January 14-15, 2013	830	<i>n.d.</i>	6,550	<i>n.d.</i>	7,040	<i>n.d.</i>	2.95	6.30	14.68	40.48	14.40	13.10	2.73	0.89	0.074
WWTP1(6)	January 15-16, 2013	750	<i>n.d.</i>	6,130	19	6,930	<i>n.d.</i>	3.07	7.07	18.04	39.38	17.44	13.93	2.53	0.81	0.082
WWTP1(7)	January 16-17, 2013	880	<i>n.d.</i>	5,460	<i>n.d.</i>	3,870	<i>n.d.</i>	2.77	7.17	47.33	48.22	17.53	15.45	2.57	0.85	0.131
RA1(1)	January 2-3, 2013	370	15	1,420	18	1,000	19	0.33	0.24	1.28	0.65	0.18	0.41	<i>n.d.</i>	<i>n.d.</i>	0.105
RA1(2)	January 3-4, 2013	440	18	1,670	24	850	22	0.36	0.25	1.69	0.58	0.42	1.11	<i>n.d.</i>	<i>n.d.</i>	0.117
RA1(3)	January 4-5, 2013	370	13	1,510	17	850	15	0.32	0.28	2.29	0.84	0.58	0.38	<i>n.d.</i>	<i>n.d.</i>	0.112
RA1(4)	January 5-6, 2013	1,520	<i>n.d.</i>	2,150	<i>n.d.</i>	1,210	<i>n.d.</i>	0.35	0.20	1.15	0.50	<i>n.d.</i>	0.23	<i>n.d.</i>	<i>n.d.</i>	0.139
RA1(5)	January 6-7, 2013	1,320	<i>n.d.</i>	7,250	18	870	<i>n.d.</i>	0.33	0.23	1.72	0.54	0.14	0.28	<i>n.d.</i>	<i>n.d.</i>	0.140
RA1(6)	January 7-8, 2013	960	<i>n.d.</i>	8,900	<i>n.d.</i>	990	<i>n.d.</i>	0.33	0.24	2.30	0.66	0.17	0.69	<i>n.d.</i>	<i>n.d.</i>	0.158
RA1(7)	January 8-9, 2013	900	<i>n.d.</i>	9,090	21	1,312	<i>n.d.</i>	0.33	0.25	1.56	0.72	<i>n.d.</i>	0.26	<i>n.d.</i>	<i>n.d.</i>	0.144
RA2(1)	December 24-25, 2012	1,760	14	560	18	610	17	0.22	0.27	1.03	0.72	0.08	0.32	<i>n.d.</i>	<i>n.d.</i>	0.198
RA2(2)	December 25-26, 2012	1,330	<i>n.d.</i>	820	<i>n.d.</i>	640	<i>n.d.</i>	0.24	0.19	0.71	0.45	<i>n.d.</i>	0.23	<i>n.d.</i>	<i>n.d.</i>	0.219
RA2(3)	December 26-27, 2012	3,780	<i>n.d.</i>	1,640	17	1,760	15	0.27	0.17	0.62	0.53	<i>n.d.</i>	0.23	<i>n.d.</i>	<i>n.d.</i>	0.215
RA2(4)	December 27-28, 2012	2,010	<i>n.d.</i>	1,140	<i>n.d.</i>	780	<i>n.d.</i>	0.25	0.15	0.46	0.39	<i>n.d.</i>	0.20	<i>n.d.</i>	<i>n.d.</i>	0.203
RA2(5)	December 28-29, 2012	630	<i>n.d.</i>	580	<i>n.d.</i>	430	<i>n.d.</i>	0.27	0.19	0.97	0.48	0.09	0.22	<i>n.d.</i>	<i>n.d.</i>	0.169
RA2(6)	December 29-30, 2012	620	<i>n.d.</i>	700	19	540	<i>n.d.</i>	0.26	0.31	0.93	0.74	0.18	0.43	<i>n.d.</i>	<i>n.d.</i>	0.143
RA2(7)	December 30-31, 2012	280	<i>n.d.</i>	670	<i>n.d.</i>	620	<i>n.d.</i>	0.24	0.34	1.07	1.18	0.21	0.41	<i>n.d.</i>	<i>n.d.</i>	0.106

Note: c(g) = concentration in gas-phase, c(p) = concentration in particle-phase, *n.d.* = not detected

Appendix F

Correlation Analysis

F1. Pearson correlation coefficient (*R*) among target compounds at WWTP1

Compounds	6:2 FTOH	8:2 FTOH	10:2 FTOH	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDODA
6:2 FTOH	-	-0.712	-0.514	-0.752	-0.087	0.050	-0.256	-0.209	-0.205	-0.275	-0.322
8:2 FTOH	-	-	0.530	0.399	0.282	-0.322	0.256	0.016	-0.037	-0.087	-0.010
10:2 FTOH	-	-	-	0.197	-0.187	-0.342	0.000	0.020	0.077	0.160	0.097
PFPeA	-	-	-	-	-0.309	-0.366	0.227	0.287	0.234	0.465	0.572
PFHxA	-	-	-	-	-	0.242	-0.134	-0.158	-0.344	-0.646	-0.630
PFHpA	-	-	-	-	-	-	0.363	-0.186	-0.249	0.155	0.057
PFOA	-	-	-	-	-	-	-	0.889	0.906	0.747	0.767
PFNA	-	-	-	-	-	-	-	-	0.944	0.818	0.815
PFDA	-	-	-	-	-	-	-	-	-	0.916	0.886
PFUnDA	-	-	-	-	-	-	-	-	-	-	0.984
PFDODA	-	-	-	-	-	-	-	-	-	-	-

F2. Pearson correlation coefficient (*R*) among target compounds at RA1

Compounds	6:2 FTOH	8:2 FTOH	10:2 FTOH	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDODA
6:2 FTOH	-	0.431	0.417	0.227	-0.760	-0.305	-0.653	-0.659	-0.474	-	-
8:2 FTOH	-	-	0.318	-0.327	0.023	0.291	0.023	-0.653	-0.190	-	-
10:2 FTOH	-	-	-	0.038	-0.394	-0.542	-0.107	-0.614	-0.492	-	-
PFPeA	-	-	-	-	-0.597	-0.469	-0.749	0.002	0.544	-	-
PFHxA	-	-	-	-	-	0.709	0.908	0.901	0.208	-	-
PFHpA	-	-	-	-	-	-	0.618	0.399	0.293	-	-
PFOA	-	-	-	-	-	-	-	0.681	-0.081	-	-
PFNA	-	-	-	-	-	-	-	-	0.239	-	-
PFDA	-	-	-	-	-	-	-	-	-	-	-
PFUnDA	-	-	-	-	-	-	-	-	-	-	-
PFDODA	-	-	-	-	-	-	-	-	-	-	-

F3. Pearson correlation coefficient (*R*) among target compounds at RA3

Compounds	6:2 FTOH	8:2 FTOH	10:2 FTOH	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDODA
6:2 FTOH	-	0.884	0.906	0.160	-0.611	-0.660	-0.477	-0.745	-0.542	-	-
8:2 FTOH	-	-	0.935	0.436	-0.575	-0.777	-0.388	0.850	-0.455	-	-
10:2 FTOH	-	-	-	0.344	-0.398	-0.529	-0.196	0.346	-0.315	-	-
PFPeA	-	-	-	-	-0.315	-0.271	-0.304	0.147	-0.193	-	-
PFHxA	-	-	-	-	-	0.812	0.908	0.830	0.976	-	-
PFHpA	-	-	-	-	-	-	0.724	0.199	0.701	-	-
PFOA	-	-	-	-	-	-	-	0.808	0.859	-	-
PFNA	-	-	-	-	-	-	-	-	0.838	-	-
PFDA	-	-	-	-	-	-	-	-	-	-	-
PFUnDA	-	-	-	-	-	-	-	-	-	-	-
PFDODA	-	-	-	-	-	-	-	-	-	-	-

F4 Pearson correlation coefficient (R) between target compounds and other air pollutants/ meteorological (Met.) data

Compounds/ Met. parameters	6:2FTOH	8:2FTOH	10:2FTOH	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
<i>other air pollutants</i>											
carbon monoxide	0.524	-0.383	-0.514	-0.528	-0.630	-0.393	-0.560	-0.515	-0.504	-0.227	-0.601
nitrogen dioxide	0.594	-0.586	-0.634	-0.650	-0.694	-0.513	-0.649	-0.665	-0.615	-0.432	-0.725
sulfur dioxide	0.002	0.238	-0.287	-0.301	-0.337	-0.237	-0.302	-0.267	-0.281	0.659	0.248
total hydrocarbon	0.236	-0.371	-0.861	-0.866	-0.845	-0.693	-0.871	-0.855	-0.868	-0.595	-0.609
methane	0.234	-0.366	-0.859	-0.863	-0.841	-0.687	-0.867	-0.851	-0.864	-0.593	-0.609
ozone	-0.197	0.626	0.023	0.018	-0.055	0.080	0.027	0.023	0.048	0.688	0.406
acrylonitrile	0.159	0.348	-0.077	-0.146	-0.155	-0.178	-0.194	-0.118	-0.182	-0.150	-0.199
chloroform	0.262	0.283	-0.493	-0.439	-0.453	-0.341	-0.459	-0.333	-0.460	-0.105	-0.050
1,2-dichloroethane	0.420	0.412	-0.227	-0.184	-0.177	-0.154	-0.224	-0.048	-0.233	-0.397	-0.372
benzene	-0.545	-0.669	-0.039	0.092	0.048	0.135	0.111	0.042	0.123	0.603	0.661
carbon tetrachloride	0.422	-0.054	-0.769	-0.617	-0.634	-0.412	-0.608	-0.523	-0.605	0.071	0.126
1,2-dichloropropane	0.575	0.393	-0.334	-0.272	-0.249	-0.175	-0.300	-0.147	-0.309	-0.492	-0.465
trichloroethylene	0.030	0.307	0.434	0.370	0.466	0.519	0.344	0.246	0.315	-0.641	-0.704
1,4-dioxane	0.332	0.479	-0.063	-0.031	-0.008	-0.125	-0.058	-0.018	-0.071	-0.441	-0.411
1,2-dibromoethane	-0.187	0.103	0.500	0.335	0.414	0.281	0.234	0.168	0.234	-0.670	-0.762
tetrachloroethylene	0.446	-0.201	-0.614	-0.557	-0.534	-0.424	-0.543	-0.414	-0.558	-0.365	-0.318
1,1,2,2-tetrachloroethane	0.367	0.483	-0.086	0.004	0.061	0.101	-0.035	0.096	-0.049	-0.667	-0.648
benzyl chloride	0.532	0.090	-0.651	-0.539	-0.499	-0.338	-0.548	-0.457	-0.556	-0.464	-0.426
1,4-dichlorobenzene	0.521	-0.156	-0.684	-0.514	-0.461	-0.289	-0.535	-0.443	-0.552	-0.474	-0.424
bromomethane	-0.078	-0.553	-0.858	-0.887	-0.878	-0.746	-0.872	-0.885	-0.874	-0.449	-0.477
acetaldehyde	0.438	0.386	-0.335	-0.288	-0.256	-0.160	-0.322	-0.222	-0.332	-0.458	-0.463
dichloromethane	0.419	0.401	-0.045	-0.086	-0.097	-0.137	-0.135	0.033	-0.142	-0.232	-0.244
vinyl chloride	-0.089	-0.011	-0.082	-0.099	-0.151	-0.103	-0.155	-0.128	-0.142	0.072	0.056
1,3-butadiene	0.398	0.477	0.162	0.137	0.129	0.167	0.100	0.245	0.106	-0.099	-0.146
<i>Meteorological parameters</i>											
wind speed	-0.353	0.709	0.535	0.565	0.542	0.528	0.554	0.575	0.564	0.612	0.522
temperature	0.284	-0.245	-0.350	-0.323	-0.293	-0.282	-0.348	-0.315	-0.330	-0.270	-0.166
relative humidity	-0.431	0.350	0.663	0.622	0.717	0.463	0.643	0.591	0.565	-0.465	0.118
solar radiation	-0.377	0.623	0.344	0.349	0.374	0.320	0.306	0.285	0.304	-0.096	-0.464
rain amount	-0.191	0.025	0.163	0.075	0.213	0.089	0.323	0.275	0.102	-0.344	-0.297

Appendix G

Air Pollutants and Meteorological Data by Pollution Control Department

G1. Concentrations of air pollutants and meteorological data during air sampling in Thailand

Date	CO (ppm)	NO ₂ (ppb)	SO ₂ (ppb)	THC (ppm)	CH ₄ (ppm)	O ₃ (ppb)	WS (m/s)	TEMP (°C)	RH (%)	SRAD (w/m ²)	Rain (mm)
January 10-11, 2013	0.8	23.8	1.5	2.7	2.3	22.3	2.0	28.3	75.2	181.1	0.02
January 11-12, 2013	0.7	14.7	1.3	2.5	2.2	30.5	2.3	28.9	72.8	172.5	0.00
January 12-13, 2013	0.7	14.0	1.4	2.5	2.2	26.7	2.2	28.0	73.4	134.5	0.02
January 13-14, 2013	0.7	15.7	1.7	2.5	2.2	21.6	2.0	26.4	75.4	80.8	0.00
January 14-15, 2013	0.9	19.5	1.6	2.7	2.4	10.7	1.7	26.1	75.9	114.0	0.00
January 15-16, 2013	0.7	16.0	1.3	2.5	2.2	19.5	1.9	27.9	74.0	119.3	0.00
January 16-17, 2013	1.1	23.4	1.4	2.8	2.5	22.8	2.0	27.3	70.0	137.4	0.20
January 2-3, 2013	1.1	20.5	2.0	-	-	32.2	1.0	26.8	69.6	153.8	0.03
January 3-4, 2013	0.9	33.8	3.1	3.3	2.9	21.7	1.8	26.4	58.5	127.2	0.02
January 4-5, 2013	0.8	26.6	2.9	2.9	2.5	40.3	2.2	27.5	59.8	161.7	0.03
January 5-6, 2013	1.0	29.7	2.2	3.0	2.7	40.5	2.0	27.3	63.5	163.6	0.00
January 6-7, 2013	1.0	32.4	2.2	2.9	2.6	37.9	2.2	28.2	56.5	179.1	0.00
January 7-8, 2013	1.0	28.4	3.1	2.9	2.6	61.5	1.9	28.8	62.0	144.0	0.00
January 8-9, 2013	1.3	30.9	2.9	3.1	2.7	45.9	1.8	28.1	63.7	169.7	0.00
December 24-25, 2012	1.5	64.8	1.8	-	-	5.2	0.4	27.4	52.1	22.7	0.00
December 25-26, 2012	1.4	64.8	1.9	-	-	5.6	0.5	28.5	54.4	22.4	0.00
December 26-27, 2012	1.4	65.9	1.4	-	-	4.3	0.4	29.9	54.3	24.0	0.00
December 27-28, 2012	1.6	64.3	1.5	-	-	4.6	0.5	30.6	55.4	24.6	0.00
December 28-29, 2012	1.4	62.0	1.9	-	-	3.6	0.3	31.2	54.2	17.4	0.00
December 29-30, 2012	1.2	54.1	0.9	-	-	4.6	0.4	31.6	52.8	29.8	0.00
December 30-31, 2012	0.8	36.6	0.2	-	-	14.0	1.2	28.1	53.2	31.3	0.00

Note: CO = carbon monoxide, NO₂ = nitrogen dioxide, SO₂ = sulfur dioxide, THC = total hydrocarbons, CH₄ = methane, O₃ = ozone, WS = wind speed, TEMP = temperature, RH = relative humidity, SRAD = solar radiation, ppm = part per million, ppb = part per billion, w/m² = watts per square meters

Source: Pollution Control Department (2013)

G2. Concentrations of volatile organic compounds ($\mu\text{g}/\text{m}^3$) during air sampling in Thailand

VOCs	Jan 2-3, 2013	Jan 4-5, 2013	Jan 5-6, 2013	Jan 6-7, 2013	Jan 7-8, 2013	Jan 8-9, 2013	Jan 10-11, 2013	Jan 11-12, 2013	Jan 12-13, 2013	Jan 13-14, 2013	Jan 14-15, 2013	Jan 15-16, 2013	Jan 16-17, 2013
acrylonitrile	0.69	1.08	0.85	1.07	1.33	1.85	1.09	0.56	0.76	1.19	2.03	0.73	0.98
chloroform	3.47	9.03	8.29	6.19	11.0	15.0	4.74	3.39	7.49	5.73	7.87	4.23	8.72
1,2-dichloroethane	0.04	0.73	0.77	0.64	0.99	1.19	0.54	0.36	0.59	0.52	1.01	0.48	0.90
benzene	1.22	1.04	0.77	0.70	0.46	0.74	0.63	0.78	1.00	1.00	0.76	0.77	0.99
CarbonTetrachloride	13.6	13.8	16.4	15.5	16.8	18.5	7.39	7.93	13.1	12.2	12.3	8.4	17.9
1,2-dichloropropane	0.08	0.41	0.56	0.46	0.71	0.65	0.36	0.25	0.36	0.31	0.54	0.32	0.61
trichloroethylene	0.00	0.03	0.04	0.05	0.07	0.03	0.22	0.04	0.05	0.02	0.13	0.03	0.12
1,4-dioxane	0.00	0.60	0.37	0.60	0.69	0.71	0.33	0.48	0.30	0.40	0.80	0.53	0.63
1,2-dibromoethane	5.21	0.44	0.94	1.89	1.80	1.32	17.7	0.56	0.70	0.66	9.39	10.8	1.65
tetrachloroethylene	0.50	0.01	0.55	0.18	0.36	0.44	0.05	0.10	0.07	0.07	0.24	0.05	0.40
1,1,2,2-tetrachloroethane	0.16	0.30	0.69	0.42	1.24	1.07	0.66	0.36	0.50	0.38	0.88	0.67	1.30
benzyl_chloride	1.59	1.14	2.13	1.66	2.62	2.02	1.11	0.89	1.20	0.99	1.35	1.24	2.36
1,4-dichlorobenzene	0.17	0.13	0.27	0.22	0.22	0.20	0.07	0.03	0.11	0.03	0.08	0.13	0.34
bromomethane	53.2	59.5	39.2	37.6	37.7	42.9	23.8	20.1	20.3	21.2	27.1	19.3	25.1
acetaldehyde	0.26	0.34	0.35	0.38	0.41	0.46	0.34	0.26	0.31	0.31	0.42	0.29	0.42
Dichloromethane	16.1	30.8	41.4	36.5	43.4	55.7	36.6	24.4	31.7	33.9	64.0	23.0	36.5
Vinyl Chloride	10.9	5.73	7.39	7.26	7.51	9.96	7.91	4.66	8.87	8.61	11.4	5.00	7.45
1,3-Butadiene	0.00	1.23	1.72	1.79	1.79	2.51	2.03	0.83	1.61	1.98	2.99	0.89	1.88

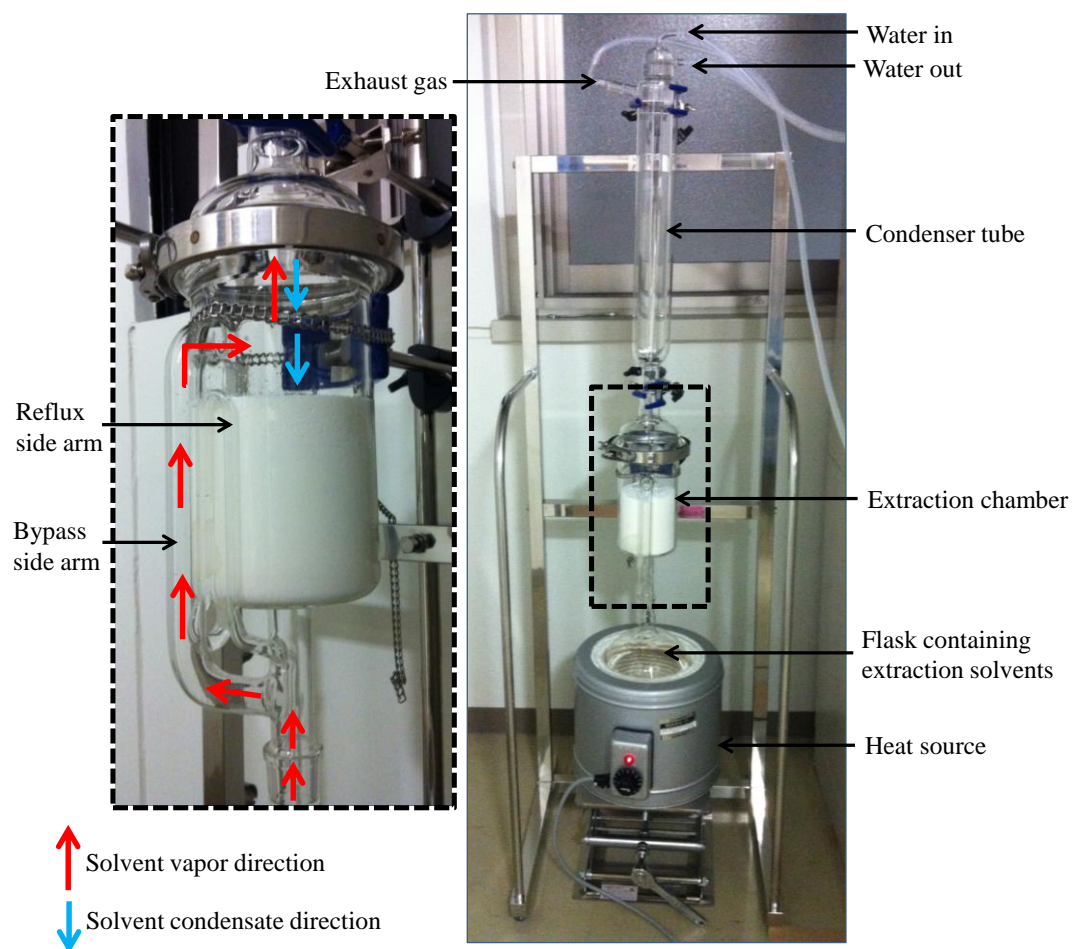
Note: VOCs = volatile organic compounds

Source: Pollution Control Department (2013)

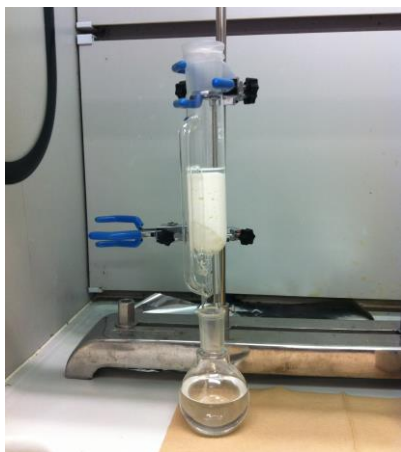
Appendix H

Soxhlet Apparatus for Cleaning and Extraction of XAD-2 Resin

H1. Cleaning



H2. Extraction



Appendix I
Concentrations of FTOHs and PFCAs in Air in Japan

I1. Concentrations of FTOHs (pg/m³), PFCAs (pg/m³) and TPM (mg/m³) at four sampling locations in air in Japan

Samples	6:2 FTOH		8:2 FTOH		10:2 FTOH		PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	TPM
	c(g)	c(p)	c(g)	c(p)	c(g)	c(p)	c(p)	c(p)	c(p)	c(p)	c(p)	c(p)	c(p)	c(p)	
A(1)-1	421,500	2,100	50,080	1,060	8,810	<i>n.d.</i>	870	141,940	1,280	27,120	290	180	150	87	0.070
A(1)-2	396,020	2,020	47,320	690	8,420	<i>n.d.</i>	1,770	239,680	1,800	40,810	480	230	220	150	0.060
A(2)-1	372,080	5,570	145,890	6,340	17,060	1,360	1,760	564,640	1,940	102,860	940	670	650	250	0.400
A(2)-2	460,110	12,120	130,660	7,540	5,240	2,380	2,000	819,360	2,200	159,760	1,750	800	860	710	0.690
A(2)-3	657,030	15,840	136,070	7,940	17,690	2,370	2,270	720,790	2,270	171,290	1,830	850	890	720	0.860
B(1)-1	9,750	100	220,700	1,860	42,230	370	220	700	840	9,790	1,050	1,250	310	190	0.043
B(1)-2	13,280	93	183,020	1,810	31,260	690	290	960	1,150	8,200	1,030	1,230	300	220	0.044
B(2)	400,610	1,920	237,030	14,300	138,120	5,950	210	530	480	2,970	260	690	120	360	0.068
B(3)-1	<i>n.d.</i>	<i>n.d.</i>	52,910	227	13,360	170	17	140	100	750	66	49	45	4.5	0.033
B(3)-2	<i>n.d.</i>	<i>n.d.</i>	72,300	220	12,350	180	17	88	73	810	38	26	21	1.4	0.025
C-1	53	<i>n.d.</i>	1,850	70	840	<i>n.d.</i>	2.5	20	4.7	130	15	3	6.3	5.6	0.040
C-2	25	<i>n.d.</i>	490	<i>n.d.</i>	250	<i>n.d.</i>	5.9	48	4.5	13	13	2	4.9	0.9	0.032
D-1	9	<i>n.d.</i>	82	<i>n.d.</i>	64	<i>n.d.</i>	0.4	18	1.8	6.2	2.7	0.6	<i>n.d.</i>	<i>n.d.</i>	0.018
D-2	7	<i>n.d.</i>	60	<i>n.d.</i>	57	<i>n.d.</i>	0.4	12	1.3	6.3	2.3	0.5	<i>n.d.</i>	<i>n.d.</i>	0.030
D-3	7	<i>n.d.</i>	55	<i>n.d.</i>	55	<i>n.d.</i>	0.5	11	1.6	5.7	2.5	0.7	<i>n.d.</i>	<i>n.d.</i>	0.029

Note: c(g) = concentration in gas-phase, c(p) = concentration in particle-phase, *n.d.* = not detected

I2. Concentrations of FTOHs (pg/m³), PFCAs (pg/m³) and TPM (mg/m³) at Site A during air cleaning

Sample	6:2 FTOH		8:2 FTOH		10:2 FTOH		PFPeA		PFHxA		PFHpA		PFOA		PFNA		PFDA		PFUnDA		PFDODA		TPM
	c(g)	c(p)	c(g)	c(p)	c(g)	c(p)	c(g)	c(p)	c(g)	c(p)	c(g)	c(p)	c(g)	c(p)	c(g)	c(p)	c(g)	c(p)	c(g)	c(p)	c(g)	c(p)	
AS1	340,540	4,700	6,500	3,140	510	<i>n.d.</i>	90	1,790	800	396,030	44	510	230	39,760	38	320	39	88	22	180	5.8	51	0.093
AS2	296,390	15,020	6,530	2,170	650	<i>n.d.</i>	21	1,710	570	276,070	66	410	260	25,480	70	67	4.9	63	13	78	16	32	0.080
AS3	206,740	32,950	7,120	1,930	990	<i>n.d.</i>	24	2,150	420	268,510	40	450	120	30,570	89	240	42	97	20	100	5.0	45	0.063
AS4	97,680	6,230	5,560	1,600	270	<i>n.d.</i>	21	2,290	470	256,000	39	460	150	24,750	27	160	14	82	19	100	4.3	29	0.067
AS5	23,160	12,680	3,410	1,150	160	<i>n.d.</i>	10	1,450	430	249,150	58	400	140	20,570	56	140	10	95	25	100	5.0	49	0.067
AS6	38,360	8,960	11,520	780	1,000	<i>n.d.</i>	10	2,070	420	191,030	77	620	120	12,040	53	140	14	110	26	140	7.0	70	0.057

Note: c(g) = concentration in gas-phase, c(p) = concentration in particle-phase, *n.d.* = not detected

I3. Amount of FTOHs and PFCAs (ng) adsorbed onto activated carbon air cleaner

Extraction	6:2 FTOH	8:2 FTOH	10:2 FTOH	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDODA
AC-R1	86,960	3,120	660	630	98,250	4.2	6,370	5.4	1.5	5.1	1.5
AC-R2	6,470	270	120	5.2	17,630	1.7	1,160	3.8	0.7	2.7	0.7
AC-R3	840	140	60	1.8	1,530	0.8	120	1.2	0.2	0.6	0.2
AC-R4	140	50	30	0.5	250	0.2	7.1	0.2	0.02	0.01	0.1

Note: AC-R1 to AC-R4 = 1st extraction to 4th extraction

Appendix J

Results of Wet Deposition and Sunlight Exposure Experiments for Water Samples

J1. PFCA Concentrations in rainwater samples in Japan for wet deposition and sunlight exposure experiment

Sample	n	Sunlight exposure	PFPeA		PFHxA		PFHpA		PFOA		PFNA		PFDA		PFUnDA		PFDoDA	
			c(l)	c(s)	c(l)	c(s)	c(l)	c(s)	c(l)	c(s)	c(l)	c(s)	c(l)	c(s)	c(l)	c(s)	c(l)	c(s)
Rain(1)-Day0	1	-	0.47	0.15	6.55	0.47	2.90	0.11	2.56	0.12	4.33	0.61	1.27	0.04	0.98	0.05	0.26	0.06
Rain(1)-1 wk	1	June 1-7, 2013	1.01	0.10	5.15	0.53	3.34	0.12	5.23	0.16	4.45	0.52	2.79	0.12	1.29	0.13	0.23	0.09
Rain(1)-4 wk	1	June 1-28, 2013	0.81	<i>n.d.</i>	10.55	0.44	5.87	0.05	4.54	0.07	7.11	0.09	3.38	0.23	1.68	0.36	0.22	0.24
Rain(2)-Day0	2	-	0.34	<i>n.d.</i>	2.71	0.57	0.78	0.10	0.91	0.10	2.23	0.12	0.18	0.06	0.17	0.04	0.05	0.04
Rain(2)-1 wk	2	June 22-28, 2013	0.18	0.15	3.18	0.65	1.07	0.09	1.07	0.09	3.14	0.11	0.16	0.08	0.20	0.04	0.10	0.04
Rain(2)-2 wk	2	June 22 to July 5, 2013	0.23	0.16	4.14	0.53	1.00	0.17	1.32	0.18	5.51	0.70	0.49	0.17	0.27	0.10	0.14	0.10
Rain(3)	1	-	0.81	2.49	8.65	1.48	4.25	0.72	3.13	0.77	3.32	1.24	0.20	0.70	0.12	0.48	<i>n.d.</i>	0.32
Rain(4)	1	-	0.47	0.58	5.22	0.80	3.10	0.42	1.30	0.50	1.02	1.00	0.08	0.19	0.08	0.18	<i>n.d.</i>	0.13
Rain(5)	2	-	0.70	0.25	5.76	0.55	1.15	0.12	1.25	0.13	0.75	0.20	0.38	0.11	0.22	0.07	0.08	0.06
Rain(6)	2	-	0.05	0.04	4.99	0.68	0.30	0.13	0.64	0.15	<i>n.d.</i>	0.16	<i>n.d.</i>	0.08	<i>n.d.</i>	0.04	<i>n.d.</i>	0.04
Rain(7)	2	-	0.22	0.14	6.10	0.80	1.21	0.13	2.72	0.15	1.18	0.18	0.23	0.16	<i>n.d.</i>	0.09	<i>n.d.</i>	0.22

Note: c(l) = concentration in liquid-phase, c(s) = concentration in solid-phase, *n.d.* = not detected

J2. PFCAs Concentrations in river water samples in Thailand

Sample	n	Sunlight exposure	PFPeA		PFHxA		PFHpA		PFOA		PFNA		PFDA		PFUnDA		PFDoDA	
			c(l)	c(s)	c(l)	c(s)	c(l)	c(s)	c(l)	c(s)	c(l)	c(s)	c(l)	c(s)	c(l)	c(s)	c(l)	c(s)
River-Day0	2	-	1.58	<i>n.d.</i>	0.14	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.58	0.06	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.08	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
River-wk1	2	December 23-29, 2013	0.79	<i>n.d.</i>	0.38	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.56	0.17	<i>n.d.</i>	0.21	<i>n.d.</i>	0.25	<i>n.d.</i>	0.05	<i>n.d.</i>	<i>n.d.</i>
River-wk2	2	December 23, 2013 to January 5, 2014	1.19	<i>n.d.</i>	0.22	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.47	0.39	<i>n.d.</i>	0.31	<i>n.d.</i>	0.30	<i>n.d.</i>	0.04	<i>n.d.</i>	<i>n.d.</i>
River-wk3	2	December 23, 2013 to January 12, 2014	6.12	<i>n.d.</i>	0.63	<i>n.d.</i>	0.11	<i>n.d.</i>	5.23	0.38	<i>n.d.</i>	0.09	<i>n.d.</i>	0.26	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
River-wk4	2	December 23, 2013 to January 19, 2014	3.48	<i>n.d.</i>	0.47	<i>n.d.</i>	0.43	<i>n.d.</i>	2.30	2.07	<i>n.d.</i>	0.56	<i>n.d.</i>	0.91	<i>n.d.</i>	0.09	<i>n.d.</i>	<i>n.d.</i>
River spike-Day0	2	-	1.50	<i>n.d.</i>	0.18	<i>n.d.</i>	0.03	<i>n.d.</i>	0.74	0.30	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.07	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
River spike-wk1	2	December 23-29, 2013	0.70	<i>n.d.</i>	0.68	<i>n.d.</i>	0.63	<i>n.d.</i>	2.55	0.10	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.12	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
River spike-wk2	2	December 23, 2013 to January 5, 2014	0.85	<i>n.d.</i>	0.54	<i>n.d.</i>	0.89	0.07	2.64	2.34	<i>n.d.</i>	0.42	<i>n.d.</i>	0.29	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
River spike-wk3	2	December 23, 2013 to January 12, 2014	6.80	<i>n.d.</i>	0.72	<i>n.d.</i>	1.39	<i>n.d.</i>	4.51	0.81	<i>n.d.</i>	0.17	<i>n.d.</i>	0.32	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
River spike-wk4	2	December 23, 2013 to January 19, 2014	5.21	<i>n.d.</i>	0.65	<i>n.d.</i>	1.53	<i>n.d.</i>	4.54	2.45	<i>n.d.</i>	0.13	<i>n.d.</i>	0.21	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>

Note: River = river water samples (no spike), River spike = river water samples spiked 8:2 FTOH 1,000 ng/L, c(l) = concentration in liquid-phase, c(s) = concentration in solid-phase, *n.d.* = not detected

J3. Concentration of 8:2 FTOH and PFCAs in *Ultrapure* water (spiked 1,000 ng/L of 8:2 FTOH) for sunlight exposure experiment

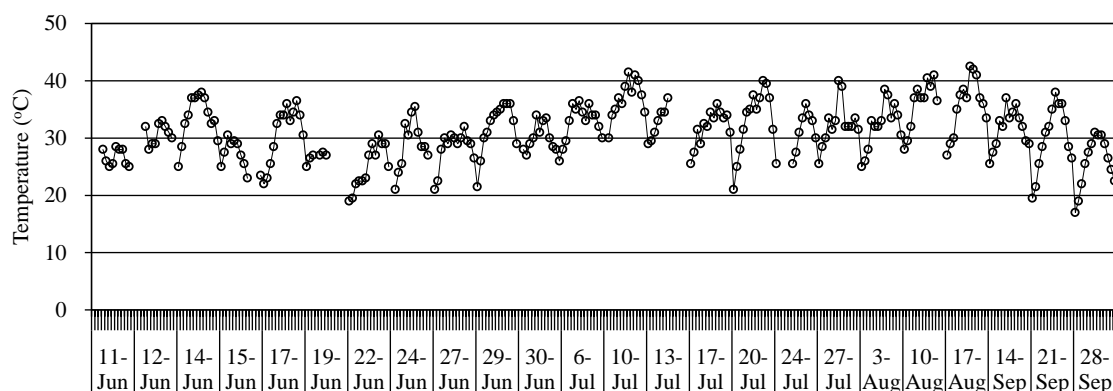
Sample	n	Sunlight exposure	8:2 FTOH	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA
UW-Day0	2	-	1000	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
UW-wk1	2	July 26 to August 1, 2013	984	0.13	0.81	<i>n.d.</i>	<i>n.d.</i>	0.96	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
UW-wk2	2	July 26 to August 8, 2013	940	0.11	0.41	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
UW-wk4	2	July 26 to August 22, 2013	849	0.09	0.39	<i>n.d.</i>	<i>n.d.</i>	0.18	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
UW-wk8	2	July 26 to September 19, 2013	751	<i>n.d.</i>	2.02	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
UW-wk12	2	July 26 to October 17, 2013	594	0.08	0.55	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
UW-control	2	Keep 25°C-no light	940	<i>n.d.</i>	0.18	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>

Note: UW = *ultrapure* water, c(l) = concentration in liquid-phase, c(s) = concentration in solid-phase, *n.d.* = not detected

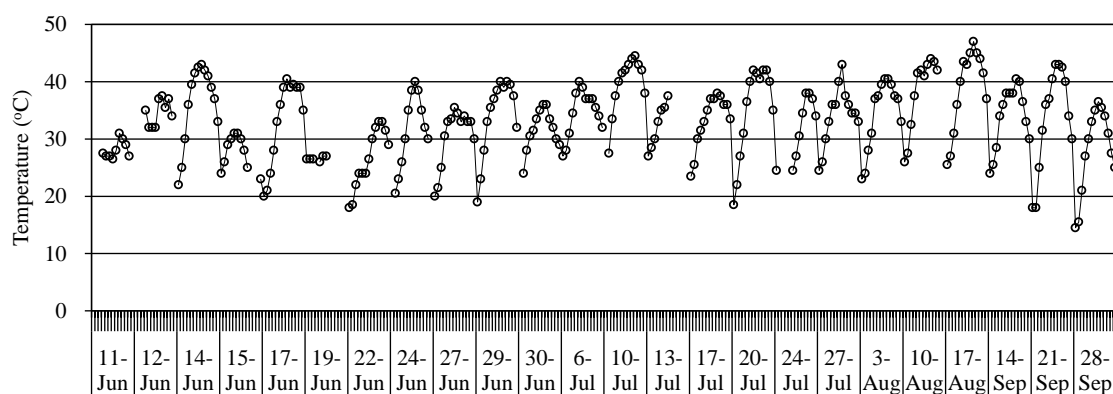
Appendix K

Temperature and Sunlight Parameters

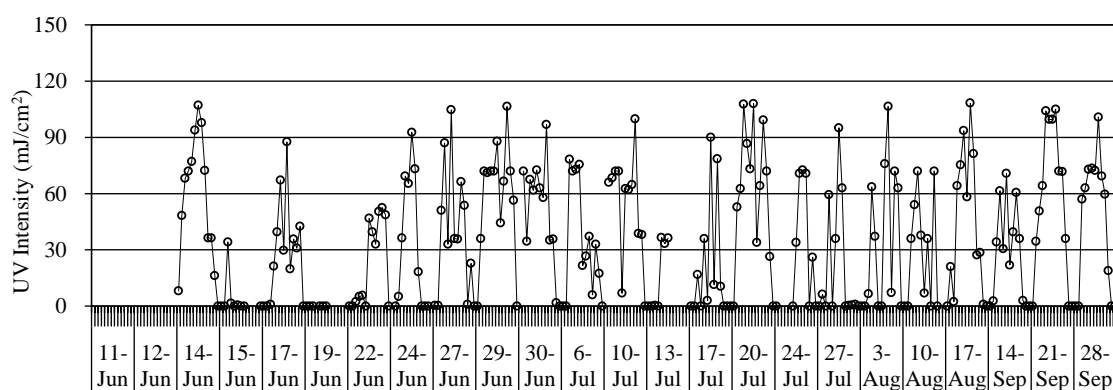
K1. Air temperatures during sunlight exposure experiment at Kyoto, Japan (2013)



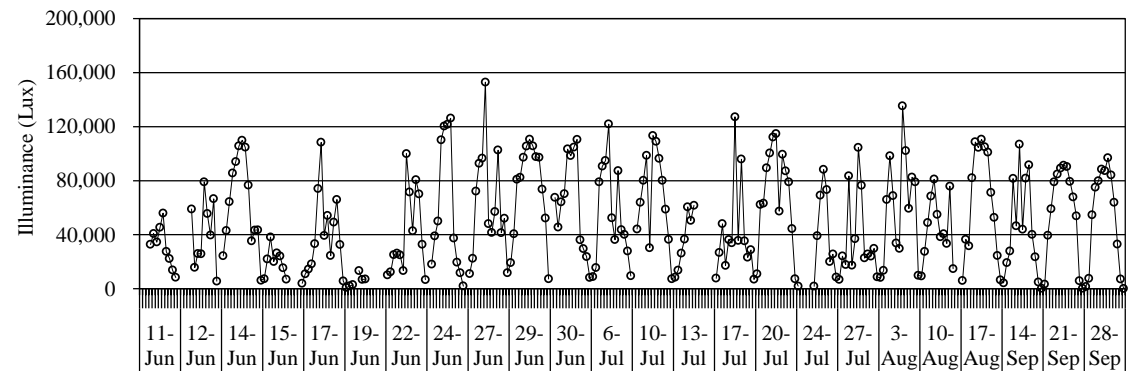
K2. Water temperatures during sunlight exposure experiment at Kyoto, Japan (2013)



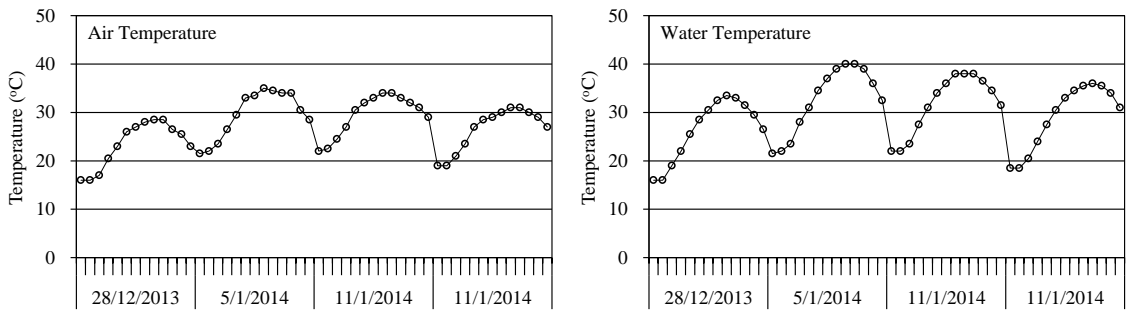
K3. UV intensity during sunlight exposure experiment at Kyoto, Japan (2013)



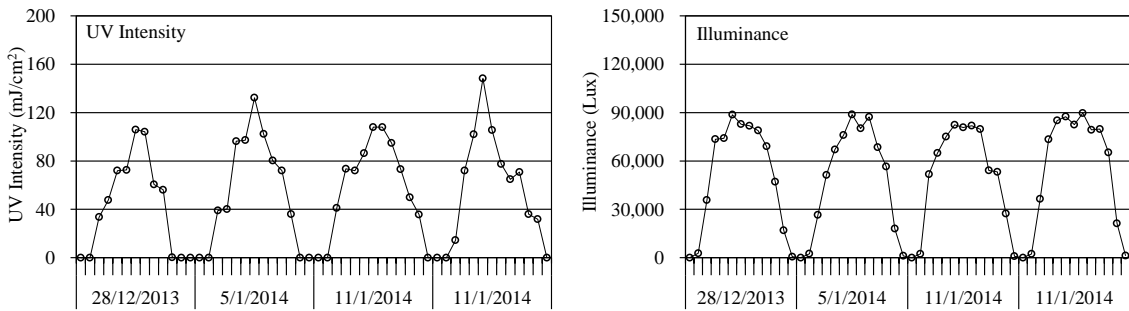
K4. Illuminance during sunlight exposure experiment at Kyoto, Japan (2013)



K5. Air and water temperatures during sunlight exposure experiment in Thailand



K6. Sunlight parameter during sunlight exposure experiment in Thailand



Appendix L

Results of UV Irradiation Experiments

L1. Initial concentration of 1,000 ng/L of 8:2 FTOH

Irradiation time (hr)	Energy (kJ/cm ²)	8:2 FTOH (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)
1	0.04	490	0.2	0.9	0.1	0.2	<i>n.d.</i>
2	0.09	400	0.1	1.8	0.2	0.4	0.1
4	0.17	340	0.2	2.5	0.9	3.1	8.7
8	0.35	60	0.3	0.7	0.5	0.5	0.3
24	1.04	<i>n.d.</i>	0.2	0.7	0.1	<i>n.d.</i>	<i>n.d.</i>

Note: *n.d.* = not detected

L2. Initial concentration of 10,000 ng/L of 8:2 FTOH

Irradiation time (hr)	Energy (kJ/cm ²)	8:2 FTOH (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)
1	0.04	5,130	0.4	0.2	0.7	3.8	<i>n.d.</i>
2	0.09	4,240	1.8	1.8	3.8	7.1	<i>n.d.</i>
4	0.17	3,400	7.1	4.9	11.9	10.1	3.2
8	0.35	1,650	9.9	9.2	17.5	11.9	0.8
24	1.04	<i>n.d.</i>	16.6	22.0	44.0	53.5	1.1

Note: *n.d.* = not detected

L3. Initial concentration of 100,000 ng/L of 8:2 FTOH

Irradiation time (hr)	Energy (kJ/cm ²)	8:2 FTOH (ng/L)	PFPeA (ng/L)	PFHxA (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)
1	0.04	70,500	2.4	5.8	8.0	18.4	0.1
2	0.09	43,830	8.6	9.9	29.5	38.6	1.2
4	0.17	21,700	39.2	33.0	106.7	93.9	3.5
8	0.35	11,840	129.7	89.0	151.7	118.1	9.9
24	1.04	1,630	191.9	160.2	216.2	140.6	9.3

Appendix M

Mass Spectrum of Fifteen TIC Peaks of the 24 Hours Irradiated Sample

